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EDITORIALS

Specialization in Manufacture

WITH exports increasing and with an unsettled state of affairs in Europe an important contributing factor to the improvement in the status of our chemical situation, it may seem absurd to be uneasy. Yet, we cannot feel secure until everything humanly possible has been done to enable that industry to gain the strength which international competition requires for lasting success. In exports the chemical industry has shown a gratifying increase, particularly in the export of coal-tar products. Recent figures from the Department of Commerce show that for the first quarter of the present year a gain of about 53 per cent has been made over the corresponding quarter of 1922. There was an increase of 50 per cent in intermediates, over 20 per cent in finished dyes, 19 per cent in medicinals, and an increase of approximately 17 per cent in the value of chemicals and allied products exported during the same period. This level may not be maintained, and it must be recognized that many of the factors contributing to the success are temporary, and that, if the position gained is to be permanent, much depends upon the chemical manufacturers themselves. Because of foreign conditions, legislation intended to be helpful has scarcely been put to the test.

Specialization in manufacture and concentration upon the development of lines for which a corporation is best fitted by training, experience, and equipment, is the thing most needed at present. Surely, the last few years have taught us much about the penalty of too rapid expansion, and the mortality among weak lines has been high. The tendency to jump into a new field which is alluring at the moment should be resisted in favor of research looking toward the production of a profitable specialty. Any other policy leads to overproduction of a few items, causes profits to vanish, and leaves industry without the complete line of quality products which constitutes one of our best defenses against importation.

Our industry is still a long way from an impregnable position. German interests are determined above all else to regain the chemical trade of America and of China, where our products now present a barrier to the attainment of that ambition. The old weapon of full-line forcing, by which the consumer is compelled to take a full line of products in order to obtain the small fraction really needed, remains powerful enough to defeat our domestic development unless our manufacturers will undertake the production of those noncompetitive items which imports show clearly are needed here but are not yet manufactured. The industry owes much to the Department of Commerce and the Tariff Commission in promptly providing detailed statistics which indicate clearly the steps to be taken in completing our program of manufacture.

Just when a division of world trade and a corresponding agreement to refrain from the manufacture of some lines of chemicals will be offered as a bait to the stockholders of American concerns, is a question. But it is something to be expected, and when it comes may prove attractive to those who have become weary in an uphill struggle. That the acceptance of such a compromise would not be in the best interests of America seems obvious. We must consent to no such limitations as would inevitably follow. But in the meantime, strength—scientific, technical, and financial—must be gained.

We must not be misled by reports of foreign conditions in the foreign press, for one man like Stinnes can exercise an enormous influence upon public opinion. This industrialist is said to control outright seventy-one different newspapers, and has also acquired the Hirsch Bureau, now known as the Telegraphic Union, which supplies articles to thousands of newspapers of all sorts. Directors of German firms have stated that new products, the result of research, will not be put upon the market so long as their plants are under the inspection and supervision of interallied chemists and technologists. They have no thought of risking the fruits of years of labor while these competitors are in commanding positions, but as soon as they are rid of this hindrance several new processes are to be introduced. This is only another proof of the fact that to stay in the running even the manufacturer of a specialty requires constant developmental work. A product perfect to-day may be obsolete to-morrow, made so by the new offering of a competitor. The well-known combination of German plants, common in all industries, continues to be a menace which cannot be combatted by a similar method here, thanks to our laws. Accordingly, the threat of a foreign monopoly is ever over us.

The manufacturer who under all these conditions calmly reviews his abilities, carefully selects his specialties, and proceeds to lay plans to excel in his own field, appeals to us as the one who will survive these uneasy times. He may not make such an immediate success as his rival who is occasionally fortunate in opportune moves, but his foundation will be secure and his structure permanent.

Fellows

THE idea of creating within our successful democratic SOCIETY a professional group to be known by some such title as "Fellows of the American Chemical Society" is by no means new or novel. A plan aiming at the same result has been before the Council on several occasions. The Proceedings for 1907, page 71, indicate that a distinguished committee, known as the Committee on Qualifications of Chemists, was appointed, and its report is to be found on page 87 of the Proceedings for 1908. A larger committee of fifteen was appointed, as recommended, to consider this subject further, and in 1909 reported: "It is the opinion of the majority of the committee that some body of the kind is desirable, but that it cannot be formed within the American Chemical Society and it is not desirable to attempt the formation of an Institute of Chemistry at the present time."

But the discussion did not end there. That membership in the AMERICAN CHEMICAL SOCIETY should be enhanced in value was a point brought out in the Council Meeting in Birmingham, when the Committee on Progress in Society Procedure was authorized. In its year's work, the committee obtained many opinions on this subject, decided that something should be done, but only after due deliberation, and with this in view recommended that the task of formulating a plan be assigned to a special committee. This committee was appointed at the New Haven Meeting and will report at

Milwaukee. It is a subject of much importance and councilors should go to Milwaukee prepared to discuss it.

The plan of having associate members seemed inadequate. It was not the right course. We believe a class of Fellows can be created that will not only enhance the value of membership for those who can qualify, but in time will bring about a situation in American chemistry that will be very helpful to our profession. Whether we approve of licensing chemists and chemical engineers or not, there are many who believe that before long there will be laws requiring the license in all the states. We have, we believe, in the AMERICAN CHEMICAL SOCIETY an opportunity so to draw the specifications for those who would be Fellows as to have such distinction qualify them for license without examination. If we can but draw our specifications with sufficient skill, we can make "Fellows of the American Chemical Society" a title as much sought after as similar titles in foreign societies. There is nothing of that sort in America to-day.

That the specifications are difficult to draw is obvious. In this work the committee, of which William Hoskins of Chicago is chairman, needs all the suggestions and constructive criticism that can be given it.

A code of ethics is also an old story for the AMERICAN CHEMICAL SOCIETY. Under the direction of the Council, A. D. Little and his committee worked for two years upon a code, only to have the Council decide that no code was required for American chemists. Since then other bodies have recognized the desirability of codes of ethics. The engineering bodies have adopted such codes, and even the American Bar Association contemplates adopting canons of judicial ethics as formulated by a committee headed by Chief Justice William Howard Taft. Surely, if judges can derive some benefit from a code of ethics for their guidance on and off the bench, there need be no hesitancy on the part of chemists in taking like action. Should ways be found for creating a class of Fellows within the AMERICAN CHEMICAL SOCIETY, we trust a strict code of ethics will be adopted, as well as some plan which provides for the disbarment of a Fellow if he should violate the code.

There will be several problems before the Council at Milwaukee, but none which presents greater difficulties than the fellowship plan. Few, if any, are more important from the standpoint of American chemistry.

The Earning Power of Research

CHEMICAL and Metallurgical Engineering, in the June 11 issue, pleads for the sale of research for what it is, with emphasis upon values other than the immediate return which, unfortunately, is of first interest to practically all boards of directors. Would that it were possible to win the support of industry for the conquest of truth for its own sake!

We know of one man of wealth who, it is said, cannot be interested in any money-making venture. He regards it as his duty properly to expend what he has in the interests of humanity. For him there is the appeal of providing means to an easier, more enjoyable, and longer life for men, the alleviation of suffering, and long-time studies aimed at the very cause of international ills. We know of another man who serves by devising labor-saving machinery. For him research can provide materials having necessary chemical and physical properties. But what of the long, long list of men who still reckon in terms of what the work will return in cash? These men must be converted to research by the appeal made through touching the purse nerve. If they are fortunate in their choice of a research director and in choosing a sufficient number of worth-while problems, and will adequately support the work in continuity, they will be won over to research for its values other than the direct cash return and continue its adherent in perpetuity.

We have approached the task of selling real research from a number of angles, and we venture the opinion that in almost every case research, and even scientific work which is not research, is undertaken either because the guardians of the treasury are convinced that it will pay in dollars and cents, or because some other such work has paid.

Research pays—of course it pays—in many ways besides cash, but as yet that means little to the average stockholder. We know it pays as insurance against the uncertainty of the future. With knowledge obtainable in no other way an industry faces forward without dread. Little by little industry has come to appreciate that the destruction of a plant by fire is as nothing compared with the loss of business to a competitor through his superior knowledge. Research attracts better men to an industry, for they know that a properly supported research laboratory is one indication of forward-looking executives. Research adds a real interest to otherwise routine work, and owners themselves find a new interest in their daily task. Research raises the intellectual level throughout an entire industry. With the advent of science, old organizations have changed, bringing in a higher type of both executive and operative.

At times research has been used to gain confidence. It has even been used as an advertisement. It has assumed such importance in some instances that a plant with a laboratory attached has been changed to a laboratory with a plant attached. We know it is worth while to establish even fragments of truth, as T. W. Richards in his AMERICAN CHEMICAL SOCIETY presidential address so ably emphasized in discussing accurate atomic weight determinations.

But those responsible for funds have too generally entered upon their careers without a proper appreciation of scientific work. They want returns and fail to understand the toil that must precede the harvest. We quote Dr. W. H. Bragg, the eminent British physicist:

> It is easy and fascinating to suppose that a new invention is found as complete and clean as a nugget of gold, as unexpected and as unconnected with its surrounding, and finally as readily convertible into cash. The truth is very different. Science does not increase by the constant addition of new facts to old, as a library collection increases by the addition of new books or a museum by the addition of new specimens and curios. Science grows like a tree which shoots out new branches continually and at the same time strengthens the old, always growing higher into the light. Like the tree, science needs wise cultivation. The nourishment of the tree, its training and pruning, have their true counterparts in science. In both, the fruits come as the reward of skill and labor.
>
> The fruits of science are first seen when they are brought to market, and it is vaguely supposed they are picked up *somewhere* and *somehow* in the condition in which they appear. Perhaps they were made by the man who carries the basket. It is not realized that the fruit comes at the end of a long process and that even a little application of science may be the result of unseen labor and growth for many years.
>
> It is not so easy to develop scientific results as to grow an orchard. The growth of science is not so much under our control as the growth of nature.

By all means sell research for what it is, and be sufficiently adroit as a salesman to emphasize that feature in it which appeals most to your prospect, but never fail to emphasize those valuable returns which do not bear the dollar sign. To urge research without reference to its earning power is something to which to look forward. To reach that point requires contact and experience with successful work.

United States of America *vs.* the Chemical Foundation

THE action against the Chemical Foundation to compel the return of patents, etc., to the Alien Property Custodian, was opened June 4 before United States District Judge Hugh M. Morris, at Wilmington, Del. Henry W. Anderson is chief counsel for the plaintiff and William D. Guthrie and Isidor J. Kresel are in charge for the defense.

The plaintiff has undertaken to prove: Notwithstanding the great powers given to the President by Congress, he could not delegate to another the executive functions vested in him by law. On this contention rests the claim that orders issued by Acting Secretary of State Frank L. Polk were void in the first instance and therefore could not be made valid by any subsequent process of ratification by the President. Furthermore, the President's confirming order was predicated, the plaintiff asserts, upon a want of knowledge of the actual facts relating to the Chemical Foundation. It is also alleged that there was conspiracy to defraud and a combination formed to buy the patents looking toward the establishment of an American monopoly in the chemical industry, and that upon these grounds this particular sale must be declared null and void and set aside. The sale, it is further declared, was not a fair sale, inasmuch as the remuneration was entirely inadequate. The Alien Property Custodian, the plaintiff claims, was in reality a common law trustee and therefore bound to obtain as much as possible at a sale; furthermore, he virtually sold to himself, which is illegal.

The defense disputes all these contentions *in toto*. In answer to the opening statement by the plaintiff, the defendant pointed out that the President had been given the absolute power of an owner over enemy property by congressional action, and that what he did with this property in the public interest could not be reviewed by the courts. Mr. Kresel stated: "I venture to say, your honor, that this is the first time in our political history that any administration, no matter what its political complexion, has sought to invoke the judicial arm of the Government in an effort to set aside a solemn act of the President taken in time of war."

When Mr. Polk testified, the court stated, in the course of the testimony, that there had been demonstrated "most clearly and forcefully the iniquity of a court of justice going into matters affecting and appealing to the discretion of the Executive or his designated agent." While the plaintiff had hoped to prove by Mr. Polk that there had been deception in persuading him to sign the original order, it appeared that he was in full possession of the facts when the order was signed, since he had examined a copy of Alien Property Custodian Palmer's report to the President on the subject and had an interview with Mr. Palmer before he signed the order. In reply to a direct question from the court as to why he had signed the order, Mr. Polk said: "Because I felt there was an opportunity to build up a real chemical industry in this country, something we had never had before." Being asked the hypothetical question whether had he known that the patents were coming under the control of an American monopoly, he would even then have approved the sale of the patents, he replied: "I would assume that the Clayton law and the Sherman law would have protected the country from a monopoly, and in view of the statement that these patents were to be licensed to all who might require them, I would have signed it."

From the testimony of the secretary of the American Dyes Institute, by which the plaintiff expected to show that there had been conspiracy, it became evident that the activities of the Institute were merely those of ordinary trade associations, and the court remarked that if the actions disclosed constituted conspiracy, every association of manufacturers should be indicted for conspiracy, since the activities were those characteristic of any trade association.

A. M. Patterson, president of the Textile Alliance, was introduced as a witness for the Government in an effort to prove the charge of conspiracy to defraud and combination, but after his testimony had been taken the counsel for the plaintiff himself moved that the Textile Alliance be eliminated from the bill of complaint, it having been shown to his satisfaction that the Alliance was not involved in such a movement.

It was emphasized by the defense that in the purchase of these patents the really valuable part of the process—namely, the "know how," which is always an element of consideration—had not passed to the new owners by the sale of the patents, and it is contended that where an Executive Order of the President is involved and public interest is inseparable from the other features of the transaction, price must be entirely secondary. The defense points out that, should the seizure and sale of these patents be set aside, they might be held to have remained the property of the original owners, to whom they might then be returned, and we should in that event have a long list of actions arising from infringements, not only with respect to the chemical patents, but the many other patents seized by the Alien Property Custodian which are not involved in this suit.

The defense further argues that the various acts of Congress clearly indicate that there was no intention to make the Custodian a trustee to operate German property for the benefit of the enemy and merely as a conservator for the enemy. In that case the Alien Property Custodian would have been piling up huge profits out of the very war which the Germans forced upon us. The intent was to give to the President the absolute power of owner over enemy property, and in disposing of the property he had in mind primarily the necessities of the country.

After outlining the experience of America when Germany undertook to dictate our foreign policy by demanding that we force Great Britain to permit cotton to reach Germany in exchange for coal-tar products for America, Mr. Kresel said:

> I wonder where we would be to-day, in the present political situation over in Europe, with France having possession of the Ruhr, with Germany having possession of the dye works, if she still had her monopoly here. I wonder if Dr. Haeuser would be writing, for the information of the President of the United States, that they would again starve our people by denying us potash, make our sick suffer, and throw our people out of work, if we did not insist upon France evacuating the Ruhr.

A sentence from Mr. Kresel's statement which aroused some discussion is the following:

> True, on the face of the bill the United States Government appears as sole plaintiff, but we shall show, your honor, that there is here an invisible plaintiff, in the person of the great German chemical trust, the so-called "Interessengemeinschaft," otherwise known as the "I. G.," and it was certainly fitting and proper that the first witness in this case should have been the representative and the spokesman of the great I. G.

We refrain from commenting upon the testimony or the argument of either the plaintiff or the defense while the case is before the court. As we go to press, it is believed that, notwithstanding the formal move on the part of the defense to throw the case out of court with the conclusion of the government testimony, the testimony and evidence of the Foundation will be taken in its entirety for the sake of a complete record, and that it will be some weeks before the case will be argued and some months before a decision will be handed down.

MATERIALS OF CHEMICAL-EQUIPMENT CONSTRUCTION SYMPOSIUM

Papers presented before the Division of Industrial and Engineering Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923. The other papers in this symposium were published in the May and June issues.

The Protection of Concrete and Other Building Materials against Water and Noxious Fumes

By **Maximilian Toch**

Toch Brothers, Inc., New York, N. Y.

STEEL, concrete, wood, and brick are the principal building materials used in factories; but in residences, office buildings, and warehouses, stone, plaster, and oxychloride compositions are also used.

Concrete

If surface area is taken into consideration, probably concrete is more largely used than all the others combined.

It is well to quote from an editorial opinion of the *Engineering News-Record* of February, 1923, owing to the many doubts as to theory and practice which were brought out at a recent meeting of the American Concrete Institute:

> First, there is a very general concern over the behavior of outdoor concrete. More and more, bad concrete is being brought to light, and the policy of suppression of facts is retreating before a demand that the cards be thrown on the table. There are all too many examples of five to fifteen-year-old concrete, placed by competent contractors and engineers, which are far from permanent and which if examined and classified might reasonably yield some information that would help in future structures. When failures have as much publicity as tests, the reasons for the principles laid down will be better appreciated.
>
> In the same category comes the well-worn subject of sea-water concrete. For years this has been the plaything of the theoretician. Concrete goes to pieces in sea water more frequently than not, but the fact that sometimes it does not points to need of a study comprehensive in scope and particularized in examination.
>
> In concrete construction several questions are not definitely answered. One is the matter of integral waterproofing, and another the desirability of chuting.
>
> It is common to decry integral waterproofing, to claim on the basis of many tests that nothing is added by the use of such materials that cannot be just as cheaply and effectively achieved by the proper procedure of normal concreting—and yet, integral waterproofing continues to be made and used in large quantities. In chuting, on the other hand, theorizing has no place. The unsuccessful attempt at Cincinnati to get some registration of opinion one way or the other on the chute problem shows why there are doubts on this question.
>
> Skepticism as to rational methods of proportioning is far less than it once was; there are signs that we are approaching some sort of solution. The problem now is to popularize methods which need simplifying and broadcasting. Doubts here are nowhere near as great as they were five years ago.

The first fact, with regard to untreated concrete, which strikes us most forcibly, is that up to 1914 the United States Navy did not have a single great dry dock in good condition, but, particularly, the Brooklyn navy dry docks had to be continually patched and repaired where they had cracked abnormally, or where the sea had leached them badly. Some authentic photographs are recorded in the article on concrete in Baskerville's "Municipal Chemistry." The five gigantic dry docks built by the Navy in Norfolk, Philadelphia, and New York, since 1912, have all been waterproofed by the integral method, and sufficient time has passed, particularly in the case of the No. 4 Dry Dock of the Brooklyn Navy Yard, which is over nine years old, to indicate that no deterioration or solution of mortar or concrete has taken place.

Sidewalks made of concrete do not receive any treatment, either by the integral or surface method, and as a rule they show up very well. This is probably due to the fact that sanding, dusting, and abrasion of the sidewalk is not noticeable.

In this climate, where the temperature variation approaches 130 degrees or more, concrete roads crack badly, as a rule, and must be filled up with a bituminous or elastic material. Before they are repaired frost usually enters and then the fissures widen. Some engineers maintain that concrete needs no integral or surface treatment whatever, if additional portland cement is added and if the workmanship is proper, but this is only partly true. In the first place, it is a question whether exact supervision can be had in large construction work, and, of much greater importance, there is the problem of chuting. Chuting saves time and labor, but sometimes, in very large operations, 20 tons of concrete are loaded on a car propelled anywhere from 100 to 1000 ft., and the contents are lifted into a chute and allowed to slide into place. Unless an integral material, which acts as a lubricator and which slightly retards, is used, bad concrete is going to result and clogging may take place; but when no proper integral material is used, the slide is wet and additional water is added to the concrete so as to make it slide—too much water to concrete is fatal. For example, in a very large government building in Washington, in which the closest supervision was had over the concrete work, the addition of too much water in the concrete of which the floors were made resulted in one of the worst cases of cracking that the writer has ever seen—in fact, every floor in that gigantic building is alligatored to a tremendous extent.

Engineers ought to look this problem squarely in the face and not theorize about how it might be done without the addition of some protective material.

You cannot build a concrete bin or building in which certain chemicals are stored unless the concrete is acid-proofed, either integrally or by means of a thorough surface application, and you cannot dust-proof and harden a cement floor, no matter what formula of cement, sand, and aggregate you devise, unless a suitable material is applied to the surface.

Steel

The protection of steel in buildings has been very much neglected since the war. Building construction is so expensive—the plasterer, the mason, and the carpenter are getting infinitely so much more than they did before the war—that the owner is inclined to take it out of the material man, and is willing to use a cheap brick, cheaper paint, and cheaper materials generally, often to his sorrow; but in a chemical works this cannot be permitted, where steam-laden fumes carry a small percentage of free chlorine or sulfuric acid, which is a common occurrence in many factories.

There is no one who can definitely say that one material will act as a panacea for all these conditions, but many of these cases have to be treated individually.

Free chlorine and the fumes of bleaching powder are so corrosive that a paint that will withstand sulfuric acid will not withstand chlorine products—in fact, in many instances it is advisable, where rust pittings are very bad, to paint the steel with a waterproof paint and then put on a 1-in. coat of portland cement grout, which of itself must be exceedingly dense, and which should then be followed with an alkali-proof, acid-proof, or chlorine-proof paint, as the case may be.

Wood

Wooden vats present a very important problem in painting. Some years ago it was the general impression that a wooden vat, whether connected with a sprinkler system on the roof of a building or used in the interior of a building, needed no coating, but looking out over the sky line of the City of New York, where practically every big building is sprinklered, and therefore has a 5000 or 10,000-gal. tank from 10 to 20 ft. above the roof, you seldom see one that has not been painted on the outside, and even if you do see one that is unpainted, the hoops are always painted. There is a simple problem in engineering which regulates why a vat should be unpainted on the inside and painted on the outside—one of tension and compression. From the writer's experience—and his firm has over 100 wooden tanks in its factory—he has found that continual painting and continual looking after the hoops save the price of many a new tank.

In alcoholic fermentation, when beer was manufactured in this country, it was found that the only material which was suitable for the painting of the interior of wooden fermentation tanks was a mixture of practically pure, acetone-free ethyl alcohol and 4 lbs. of the highest grade of East India shellac, known as "DC" or as "VSO," and because only between 3 and 5 per cent of alcohol was generated, the coating was not affected and withstood the action of the mash for about six months.

It was subsequently found, however, that this mixture, which was known throughout the trade as "brewers' varnish," was expensive to apply, and a great many objected to it on account of the alcoholic fumes.

Since then a much better material has been placed on the market, which is in the form of a wax. It is unaffected by acids, alkalies, or alcohols, and is harmless to the workman who applies it, because it contains no volatile matter. This appears to be a very high grade of resin copal, similar to kauri, which has been melted with some form of wax, and when this material is applied with a blow torch and thoroughly impregnated into the interior of the tank, it has been known to last for four or five years.

Chemical manufacturers have adopted materials of this type for the interior of vats, and experiments show that both strong vinegar and hydrochloric acid have no effect on a coating of this type.

Brick and Hollow Tile

Brick and hollow tile should either be painted or should have a colorless application where the original texture is to be preserved.

In the last few years we have made so many advances in the treatment of tung oil that these colorless coatings are to be had in endless varieties.

A camera which occupies two rooms of the Department of the Interior building is now used for photographing maps of the United States, maps of oil fields, and charts showing mineral resources. The lens, bellows, and copy-holder are in one room, and the plate-holder and dark room are in the other room. The camera will take a picture one yard square. It weighs 7000 lbs. and is operated either by hand or by electricity. Focusing is done by means of an electrical contrivance.

The Resistivity of Various Materials towards Photographic Solutions[1]

By J. I. Crabtree and Glenn E. Matthews

Eastman Kodak Co., Rochester, N. Y.

Although much information is available in the literature concerning the effect of alkalies, acids, and numerous other solutions on materials which might be suitable for constructing trays, tanks, film holders, etc., for photographic purposes,[1,2,*] very little of this information throws any light on the probable effect of photographic solutions on these materials.

The suitability of a material from a photographic standpoint depends on two factors—namely, the resistivity of the material to the action of the photographic solution, and the effect of the material on the useful life of the solution. The second factor is of great importance, since a solution such as a developer may appear unchanged after a week's exposure to a metal, but on testing the developer may be found to fog emulsions badly. In this event the metal would be entirely unsuitable for constructing developing apparatus, but it might be satisfactory for fixing, washing, or toning apparatus. A material which is resistant and does not produce undesirable effects with any photographic solution is, of course, to be preferred.

Of the possible materials suitable for constructing photographic apparatus, the following were considered:

1—Metals, plated metals, and alloys
2—Nonmetallic materials
  - Enameled steel
  - Glass
  - Impregnated fibrous materials
  - Lacquered metal
  - Porcelain and glazed earthenware
  - Rubber, rubber composition, and nitrocellulose materials
  - Slate and alberene stone
  - Wood

Metals, Plated Metals, and Alloys

The ductility of metals and alloys and the fact that they can be readily soldered and welded would seem to render them particularly suitable for the manufacture of photographic apparatus; although to date no satisfactory metal or alloy is known which is entirely suitable for use with all photographic solutions, it is necessary to restrict their use to specific purposes.

Fixing baths are the most corrosive on account of their frequently high acidity, and in a used bath, if any metal less noble than silver is immersed therein, silver is deposited on the metal and an equivalent quantity of the metal goes into solution. Such a coating of silver usually renders the metal more resistant, though if the under layer of metal is exposed to an acid solution free from silver, electrolytic corrosion sets in. Pure silver is satisfactory except for toning solutions. Lead has been extensively used for lining wooden tanks and trays, and has proved satisfactory except for some toning solutions, while lead-coated steel[3,4] offers promise. Zinc has been used for washing tanks and is fairly satisfactory for this purpose. Pure tin has long been employed for conveying distilled water. Nickel-plated brass is satisfactory for small developing tanks when they are used intermittently, but plated metals invariably corrode in contact with fixing solutions. Thus, a nickel-plated copper rack for holding photographic plates fell to pieces.[5]

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[1] Communication No. 176 from the Research Laboratory of the Eastman Kodak Company.

[*] Numbers in the text refer to the bibliography at the end of the article.

Discolored solutions are often produced by a reaction between the metal and the developing or fixing solution, and in time stain the gelatin film. Thus, iron forms purple stains with a pyro developer.[5]

Although numerous alloys have appeared during the past few years,[6,7] Monel metal is the only one which has been adopted to any extent for photographic use, and this alloy is not entirely resistant to acid fixing solutions.

In order to obtain data as to the relative resistivity of various metals, plated metals, and alloys, the following were examined:

METALS
Aluminium
Copper
Iron
Lead
Nickel
Tin (block)
Zinc

PLATED METALS
Galvanized iron
Tinned iron

ALLOYS
Aterite No. 136 (Cu-Ni-Zn)
Brass (commercial sheet)
Duriron
Monel
Niaco (Ni alloy)
Nickel Silver (Cu-Ni-Zn-Fe)
Nicolene (Ni-Cu)
Phosphor bronze (Cu-Sn-P)
Solder A (80% Pb-20% Sn)
Solder B (20% Pb-80% Sn)
Rezistal steel (Cr steel)
Type metal (Pb-Sb)

These metals and alloys were tested with the following photographic chemicals:

1—*Developers.* (NOTE: The formulas are expressed in abbreviated form—namely, the number of grams of each constituent in a liter of solution ready to use—arranged in the following order: reducing agent, sodium carbonate (dry); sodium sulfite (dry); potassium bromide.)

(*a*) Elon-hydroquinone (low elon content)	Elon 2.3 Hydroquinone 9.2–48–96–2
(*b*) Elon-hydroquinone (high elon content)	Elon 4.0 Hydroquinone 1.0–20–10–0.5 Sodium bisulfite 10
(*c*) Pyro (two solution)	Pyro 10–37.5–35–0.5 Sodium bisulfite 8.5

2—*Fixing Baths.*

(*a*) 30 per cent hypo solution

(*b*) Acid hypo solution (formula in grams per liter)

Hypo	Sodium sulfite	28 per cent acetic acid	Potassium alum
300	4.5	25 cc.	3.0

(*c*) Partially exhausted acid hypo solution (*b*) containing dissolved silver

(*d*) Completely exhausted acid hypo solution (*b*) containing dissolved silver

3—*A hypo-alum Toning Bath,* containing potassium alum, hypo, silver nitrate, and sodium chloride.

4—*Water.* Information as to the effect of moisture on the materials was desired in order to determine the most suitable metal or alloy for constructing washing and rinsing tanks.

5—*Dilute Acids.* The photographer often has occasion to use solutions of dilute acids, and a number of the metals and alloys were tested to determine their relative resistance to dilute nitric and sulfuric acids.

EXPERIMENTAL DETAILS—Strips of metal, 2 x 4 in. and approximately 20 gage in thickness, were placed in 250-cc. Pyrex beakers containing 200 cc. of solution. Usually, duplicate sets were made up, keeping one set at room temperature, 65° to 70° F., and the other at a tropical temperature, 110° to 120° F. Examination was made at the end of 24 or 48 hrs., 1 wk., 2 wks., and if the test was of sufficient interest it was continued for a longer period. The volume was kept constant by adding water at regular intervals.

In each case, the following observations were made:

1—*Appearance of the Solution.* In the case of developers, the fog, which was produced on motion picture positive film after 15 min., was measured by means of the usual type of densitometer.

2—*Effect on the Metal.* Inspection was made with the aid of a microscope.

EFFECT OF DEVELOPERS—In general, it was found that metals or alloys containing either copper or tin produce excessive fog with developers. From this standpoint, the following are unsatisfactory: copper, tin, tinned iron, brass, phosphor bronze, and Solders A and B. Several of the metals and alloys, especially aluminium, iron, galvanized iron, Duriron, and Rezistal steel, were not visibly corroded, and the developer in which they were immersed did not produce fog, but the solutions were badly discolored and would no doubt stain emulsions. Of the remaining metallic materials, the most satisfactory were lead, nickel, Aterite No. 136, Niaco, Nicolene, nickel silver, Monel, and type metal. The developer solutions in which these metals had been immersed were not objectionably changed in appearance, did not fog, and exhibited only a slight corrosive action on the metals.

The results obtained with the first elon-hydroquinone developer (*a*) after one day and at the end of a week at a temperature of 110° F. are given in Table I. Tests made with Developers *b* and *c* confirmed these results.

TABLE I—ELON HYDROQUINONE DEVELOPER *vs.* METALS AND ALLOYS
(Temperature, 110° to 120° F.)

Abbreviations:
Condition of Solution: D, darker than blank; L, lighter than blank; MD, much darker than blank; NC, no change; Ppt., precipitate.
Condition of Metal: C, corroded; Dp, deposit on surface; E, etched; S, stained; U, unchanged.

	24 HRS.			ONE WEEK		
	Condition of		Fog	Condition of		Fog
METALS	Solution	Metal	Density	Solution	Metal	Density
Tin	Ppt.	U	1.26	Ppt.	E	0.76
Copper	NC	E	0.50	D-Ppt.	E-C	0.41
Aluminium	D-Ppt.	Dp-E	0.23	D-Ppt.	Dp	0.09
Zinc	D	Dp	0.22	D	E	0.14
Nickel	NC	U	0.20	NC	U	0.14
Lead	D	U	0.19	D	U	0.10
Iron	D	U	0.18	MD-Ppt.	U	0.14
PLATED METALS						
Tinned iron	NC	E	0.70	L-Ppt.	S	0.24
Galvanized iron	NC	S E	0.18	D	S	0.14
ALLOYS						
Solder B	NC	E	2.50	L Ppt.	E	1.60
Solder A	NC	U	2.50	L-Ppt.	E	1.40
Brass	D	Dp	0.30	D-Ppt.	Dp	0.45
Phosphor bronze	D	S-Dp	0.41	D	S	0.38
Rezistal steel	NC	U	0.33	D-Ppt.	U	0.26
Type metal	L	E	0.34	L	E	0.24
Duriron	NC	U	0.31	D	U	0.28
Aterite No. 136	L	S	0.22	L	S	0.16
Nickel silver	L	S	0.26	L	S	0.24
Nicolene	L	U	0.28	L	U	0.20
Niaco	NC	U	0.22	D	U	0.20
Monel	NC	U	0.20	Ppt.	U	0.12
Blank	Clear amber color		0.26	Clear deep straw Slight ppt.		0.18

EFFECT OF THE ADDITION OF METALLIC SALTS TO DEVELOPERS—As a corroborative parallel to the work carried out with developers and metals and alloys, the effect of adding the following metallic salts to the developer was studied: $Al_2Cl_6.12H_2O$; $CuCl_2$; $FeCl_3$; $NiCl_2$; $Pb(C_2H_3O_2)_2$; $SnCl_2$; $SnCl_4$; $ZnCl_2$; and $Zn(C_2H_3O_2)_2$. Two sets of experiments were conducted using Developer *a*. In the first group of experiments the salts were added so as to give concentrations of 0.1 g. per liter of developer, and in the second group, 1.0 g. per liter. The results checked very well with those found with the actual metals and alloys. Of the salts examined, only copper and stannous tin produced fog, the latter exhibiting the most fogging action, even producing fog slightly above that of the blank in concentrations as low as 0.01 g. per liter.

The fogging action of traces of copper or stannous salts is especially noticeable when developing film on a reel. The precise action of a copper salt in causing fog is not thoroughly understood—presumably it acts as a catalyst in accelerating the rate of oxidation of the developer, and it is well known that developer oxidation products cause fog. Stannous salts reduce the unexposed silver grains of the emulsion to metallic silver, which constitutes the fog.

EFFECT OF METALLIC COUPLES ON THE RATE OF CORROSION—In the course of a series of tests on metal tanks of a copper-nickel alloy, X, soldered on the inside with lead-tin solder, it was observed that if a developing solution remained in the tank for a short time the developer gave very bad fog. The cause of this excessive fogging action was traced to the presence of tin in the developer, which was the result of the tin constituent of the solder passing into solution. It was observed that the developer did not oxidize as rapidly as a corresponding developer stored in a glass tank, which would indicate that the tin was present in the stannous condition, thus protecting the developer from aerial oxidation. (The effect of stannous chloride on the keeping qualities of a developer was observed by Desalme.[8]) As a result of this observation, tests were made to determine if electrolysis was responsible for the rapid dissolving of the tin, as follows:

A strip of Alloy X and a similar strip of Solder A (low tin content) were placed in a beaker containing Developer *a*, the metals being insulated from each other. A similar beaker was prepared with the metals connected externally by means of a copper wire. A further test was made with Solder B (high tin content). Fog tests were made with the developers at periodic intervals, and it was found that if the metals were not in metallic connection within a week the developer gave only a slightly increased fog, whereas if the metals were externally connected the developer gave very bad fog. The fog measurements were as follows:

FOG DENSITY

	6 Hrs.		24 Hrs.		48 Hrs.	
	C	U	C	U	C	U
Solder A–Alloy X	3.00	0.74	1.78	0.66	1.77	0.51
Solder B–Alloy X	2.29	0.75	1.97	0.31	2.12	0.25
Blank	0.20		0.04		0.04	

C = Connected
U = Unconnected

The falling off in the fogging action with time was attributed to the oxidation of the stannous salt to the stannic condition.

Fuller experimental details will be given in a future paper on the effect of electrolysis on the rate of corrosion of metals in photographic solutions.

The practical application of these experiments is as follows: Tin and copper or alloys containing these metals should not be used in metallic contact with a more noble metal in the presence of developing or fixing solutions. For instance, a lead-lined tank should not be soldered, but should be lead-burned, and the same applies to lead piping—that is, the joints should be "wiped" and not soldered. In the case of the metal tanks above where the joints were soldered on the outside, no developer fog was produced.

EFFECT OF FIXING BATHS—An acid fixing bath is very corrosive, and as far as is known no metal or alloy has yet been found which under all conditions is resistant to fixing baths. The metal or alloy to be satisfactory should withstand the following tests:

1—It should be free from corrosion after two weeks' contact under tropical conditions with either fresh or exhausted fixing baths.

2—It should not produce undesirable changes in the appearance of the bath, such as (*a*) precipitation of dissolved constituents, (*b*) formation of foam or scum at the surface of the solution, or (*c*) objectional discoloration of the bath.

Any loss in the rate of fixation which was caused by any of these effects would be sufficient reason for rejection of the the material.

Tests made with the four different fixing baths previously described may be summarized as follows:

1—Lead, nickel, Niaco, monel, type metal, and Rezistal steel are fairly satisfactory. With lead, nickel, brass, and Monel in partially and completely exhausted fixing baths, a layer of silver plates out of the solution on the metals.

2—Copper, iron, tin, tinned iron, Duriron, nickel silver, phosphor bronze, and Solders A and B are attacked to a varying extent. They discolor the bath, and enough precipitation occurs to cause them to be undesirable.

3—Aluminium, zinc, galvanized iron, Aterite No. 136, and Nicolene are very unsatisfactory. All corrode badly, the fixing baths are covered with a thick scum, and heavy precipitates are formed. (The effect of electrolysis on the rate of corrosion of metals and alloys in fixing baths will be dealt with in a future paper.)

The results obtained with a partially exhausted bath (*c*) and comparable with those found with the other fixing baths are given in Table II.

TABLE II—PARTIALLY EXHAUSTED FIXING BATH *vs.* METALS AND ALLOYS

Abbreviations

Condition of solution: NC, no change; F, foam on surface; Ppt., precipitate; H. ppt., heavy precipitate; D, darker than blank.

Condition of metal: BC, badly corroded; C, corroded; Dp, deposit on surface; E, etched; In, incrustation; SE, slightly etched, S, stained.

(R) = Test made at room temperature.

	24 HRS. Condition of		ONE WEEK Condition of	
	Solution	Metal	Solution	Metal
	Room Temperature (68° F.)			
METALS				
Aluminium	F-Ppt. of Ag	E	D-F-H. Ppt.	C-Dp
Zinc	F-Ppt. of Ag	C	D-F-Ppt.	C-Dp
Iron	Black ppt.	Dp	D-Ppt.	Pasty Dp
Tin	White ppt.	S-SE	H. ppt. Gray	SE-Dp
Copper	Black ppt.	Dp	D (blue)-Ppt.	Thick Dp
Lead	Slight ppt.	Dp	Ppt.	Thin Dp
Nickel	NC	Dp	Ppt.	Dp
PLATED METALS				
Galvanized iron	F-D-H. ppt. of Ag	C	Thick F-H. Ppt.	BC-Black Dp
Tinned iron	NC	Dp	Ppt.	Brown-Dp
	Tropical Temperature (110° F.)			
ALLOYS				
Nicolene	F-D-H. ppt. Ag	C-Dp	Black ppt. Ag	BC-Dp Ag plated
Aterite No. 136	Ppt.	E-Polish gone	H. ppt. Black	BC-Dp
Nickel silver	NC	White Dp	Light green ppt.	SE - Rough plating Ag-blistered
Solder A	Ppt.	Thin Ag plating	H. ppt.	Black Dp
Solder B	H. ppt.	Brown Dp-Ag plating	H. ppt.	SE-Black Dp
Duriron	D	Black Dp	D-ppt.	Black Dp
Phosphor bronze (R)	Light ppt.	Dp-In	Ppt.	Black Dp
Type metal	D-ppt.	Brown Dp-Ag plating below Dp	H. ppt.	S-Dp
Brass (R)	NC	Dp	NC	Black Dp
Rezistal steel	D-Ppt.	S-Ag plate	Milky black ppt.	Dp - Rust near surface
Niaco	Pale green	White Dp	Ppt.	Black Dp-SE
Monel (R)	NC	Thin Dp	NC	Dp
Blank	Light yellow ppt. of sulfur		Light yellow Slightly heavier ppt.	

EFFECT OF HYPO-ALUM TONING BATH—Almost all the metals and alloys tested exhibited a vigorous and undesirable reaction with the hypo-alum toning bath. The experiments were conducted for one week at a temperature of 110° to 120° F., or approximately at the temperature at which the bath is recommended for use.

The reaction was evidenced by corrosion of the metal, a darkening of the precipitated sulfur in the solution, and the deposition of colored oxides and sulfides on the surface of the metals and the container. Lead, nickel, and Monel were least affected, but even these metals are not entirely satisfactory with toning baths. Aluminium, copper, zinc, brass, phosphor bronze, and galvanized iron showed visible corrosion.

These experiments confirm the experience of Crabtree and Bullock,[9] that "a hypo-alum bath in contact with pure lead for one week is slower in action and produces stains, especially on the back of prints. In general, a metal which combines at all readily with nascent sulfur or which displaces silver from its thiosulfate is not suitable as a container for hypo-alum toning baths."

For toning solutions, glass, porcelain, or enameled apparatus are to be recommended rather than metallic containers.

The results found with the hypo-alum toning bath over one week at a temperature of 110° to 120° F. are indicated in Table III.

EFFECT OF WATER OR MOISTURE—After exposure to tap water for one week at 100° to 120° F., the following metals were slightly corroded and the water in which they were immersed was filled with varying quantities of precipitates: aluminium, iron, zinc, galvanized iron, and tinned iron. Iron

TABLE III—HYPO-ALUM TONING BATH vs. METALS AND ALLOYS
(Temperature 110° F.)

Abbreviations:

Condition of solution: D, darker than blank; H. Ppt., heavy precipitate, L, lighter than blank; NC, no change, Ppt precipitate; Soln., solution.

Condition of metal: BC, badly corroded; C, corroded; Dp, deposit; E, etched; In, incrustation; S, stained; T. Dp., thick deposit.

	24 HRS.		ONE WEEK	
	Condition of		Condition of	
METALS	Solution	Metal	Solution	Metal
Aluminium	D-H. Ppt.	C-In	H. Ppt.	BC-Dp
Zinc	Ppt.	C	H. Ppt.-Soln. pale pink	BC-Dp (pink)
Copper	D-Ppt.	Black In	D-H. Ppt.	T. Dp. (crystalline)
Iron	D-Ppt.	Gray Dp	H. Ppt.	Dp (red)
Lead	D-Ppt.	Black Dp	D-H. Ppt.	Grey Dp
Nickel	NC	Thin Dp	Soln. pale green	Dp
PLATED METALS				
Galvanized iron	D-Ppt.	C-Zn coating removed	L-Ppt.	BC-T. Dp.
Tinned iron	Brown ppt.	Brown Dp.	Soln. yellow H. Ppt.	Dp (yellow)
ALLOYS				
Phosphor bronze	D-Ppt.	Powdery Dp.	Black Ppt.	C-T. Dp.
Brass	D-Ppt.	S-Dp.	D-H. Ppt.	E-T. Dp.
Monel	D	Thin Dp.	Soln. pale green	Black Dp
Blank	Partly filled with ppt. of sulfur		Soln. darker gray ppt.	

and tinned iron were the most corroded. Copper, lead, nickel, Monel, and phosphor bronze were unchanged.

EFFECT OF DILUTE ACIDS—Several of the metals and alloys were tested with solutions of 5 per cent nitric acid and with 5 per cent sulfuric acid for one week at 110° to 120° F. The strips were examined after 24 hrs. and at the end of the week. As a rough indication of the relative attack of the two acids, the metal strips were weighed before and after the tests. The results, computed on the basis of the loss in grams per 100 sq. in. of immersed surface per day, are given in Table IV.

TABLE IV—EFFECT OF DILUTE ACIDS ON SEVERAL METALS AND ALLOYS
(Results indicated as the loss in grams per 100 sq. in. per day)

5 Per cent Nitric Acid		5 Per cent Sulfuric Acid	
Lead	10.3	Iron	11.4
Tin (block)	9.4	Galvanized iron	10.9
Galvanized iron	5.8	Zinc	8.9
Nickel	3.1	Copper	1.1
Zinc	2.9	Aluminium	0.89
Brass	2.7	Phosphor bronze	0.69
Iron	2.2	Nickel	0.69
Copper	1.8	Tin (block)	0.69
Phosphor bronze	1.1	Monel	0.69
Monel	0.45	Brass	0.22
Aluminium	0.22	Lead	None

In general, the metals and alloys were attacked more strongly by 5 per cent nitric acid than by 5 per cent sulfuric acid. Aluminium, phosphor bronze, and Monel were least affected by both acids. Lead was very badly corroded by dilute nitric, but gave no loss in weight with dilute sulfuric. Nickel was corroded by nitric, but was only slightly etched by sulfuric. Galvanized iron and iron were badly corroded by each acid. On the whole, Monel metal was least attacked.

NONMETALLIC MATERIALS

ENAMELED STEEL—Enameled steel, or so-called glass-coated steel, is extensively used for constructing small trays and tanks, and has proved fairly satisfactory, although the vitreous coating is relatively brittle, and readily chips away if roughly handled. When the undercoating of steel is thus laid bare, it corrodes very rapidly and the vessel is rendered useless. The coating of enamel is resistant to weak acids used in photographic practice, but with developers and alkaline solutions the surface of the coating becomes etched and roughened. It is then difficult to clean and will be permanently discolored by solutions of dyes. Enameled steel is very satisfactory for constructing small developing and fixing tanks. If the tanks are thickly coated and are not moved about, the tendency for the enamel to chip is reduced to a minimum.

GLASS—This is undoubtedly the most satisfactory material known to-day, but owing to its fragility it is not satisfactory for large tanks or trays. Glass apparatus should be well annealed, free from ribs, and the corners of trays and tanks rounded off so as to facilitate cleaning. For containing strong alkalies, resistive glass such as Pyrex should be used.[10]

IMPREGNATED FIBROUS MATERIALS—Such materials consist of paper, wood, canvas, etc., impregnated with varnish, wax, shellac, or phenol condensation products (Bakelite, etc.). The impregnation is usually carried out by heating *in vacuo*, and then injecting wax or varnish under pressure. Trays or tanks prepared from impregnated paper or other fibrous material develop cracks with use, thus permitting access of the solutions to the under layers which are less completely protected. Such trays and tanks are entirely unsatisfactory for use with solutions containing strong alkalies or for fixing baths which are apt to disintegrate the fibrous material through crystallization as explained under "Porcelain and Glazed Earthenware."

Wood impregnated with paraffin wax is very satisfactory except in hot weather when the wax is liable to soften.[11]

An ingenious method of protecting metal ware such as tanks or troughs consists of first coating the surface of the metal with cloth or canvas, using glue as an adhesive, then brushing over with molten paraffin wax (high melting point), and finally smoothing off the surface with a hot iron. If the tank is rigid such a coating will withstand alkali or acid bleaching solutions, such as acid permanganate.

LACQUERED METAL—The commonest and most satisfactory photographic lacquer consists of asphalt or a mixture of asphalt with rubber cement, the latter serving to overcome the slight brittleness of the asphalt coating. Baked japan is very satisfactory, but none of these materials will resist developing solutions containing a high percentage of alkali. Freshly applied asphalt will often produce a scum on the surface of a developer.

PORCELAIN AND GLAZED EARTHENWARE—Many varieties of these materials exist, ranging from white china ware to glazed tile material. White porcelain is usually unsatisfactory, because the glaze invariably cracks, forming minute fissures into which hypo solution penetrates, and on drying the crystallization of the hypo or other chemicals expands the fissures, causing disintegration in a manner similar to that of ice in the weathering of rocks. This is especially true in the case of open hypo tanks, when the solution creeps up the sides of the tank, and it applies also to all biscuit ware, which is incompletely glazed or if the glaze is cracked. Tanks are now available of dark brown earthenware glazed on both sides, which are entirely satisfactory for containing photographic solutions, except very strong alkalies. They are especially recommended for storing ordinary developing and hypo solutions.

RUBBER, RUBBER COMPOSITION, AND NITROCELLULOSE MATERIALS—Hard rubber will withstand practically all photographic aqueous solutions at normal temperatures, except oxidizing solutions. Hard-rubber tanks are somewhat brittle, tend to buckle out of shape in hot weather, and are comparatively expensive. Nitrocellulose is open to practically the same objections. Rubber compositions usually consist of siliceous earth mixed with pitch, asphalt, or crude oil wax, molded under heat and pressure. Such materials are relatively brittle, warp under heat, and when used as containers for salt solutions they disintegrate in the same manner as porous earthenware. The tendency for this disintegration to occur is much less if an excess of binder is used so that the tanks or trays have a smooth surface. If the material has a rough surface or becomes etched, the crystals obtain a better grip on the walls and more strain is exerted in the process of crystallization, thus causing more rapid disintegration.

Rubber sheeting and rubberized cloth is often used for coating the inside of wooden developing trays and troughs, and is very satisfactory provided the rubber is of good quality and free from excessive filling material. For handling long lengths of wide film (Cirkut film) a rubberized wooden tray is ideal. Since solutions used in a tray or trough are usually discarded after use, they are in contact with the rubber for only a relatively short time, and therefore more corrosive solutions can be used than in the case of a rubber-lined tank.

Cheap rubber sheeting or tubing which contains excessive filling material, antimony sulfide, and free sulfur is entirely unsuitable for use with developing solutions, because the alkali in the developer reacts with the sulfide forming thioantimoniate, which produces very bad chemical fog. Pure gum rubber is quite satisfactory.

SLATE AND ALBERENE STONE—These materials are very suitable for constructing large tanks for containing developing solutions. Alberene stone is quite satisfactory for containing fixing solutions, but slate is apt to split along planes of cleavage as a result of crystallization, as previously described.

WOOD—Wood, such as cypress, is extensively used for constructing large tanks for handling roll and motion picture film. Teak is used for smaller tanks. Wood is satisfactory for developing, fixing, and washing purposes, and is cheaper than any other available material. It has the disadvantage that unless strongly braced the tanks have a tendency to warp, and in many localities fungous growths accumulate on the outside of the washing tanks and must be frequently removed. The insides of the tanks, especially wash tanks, have a propensity to accumulate slime. Wood also has the disadvantage that it becomes permanently discolored by solutions of dyes or other colored chemicals.

Wood should not be painted, because alkaline developing solutions soften the paint and ultimately cause it to flake off.

PRACTICAL APPLICATION OF RESULTS

When selecting a material suitable for constructing any particular piece of photographic apparatus, several factors should be considered, namely:

1—The resistivity of the material to the most corrosive liquid with which it will come in contact. For instance, a well-galvanized iron tank is quite satisfactory for washing purposes, but not for containing fixing baths. A lead-lined tank is quite suitable for fixing baths but not for toning baths, because most metals are affected by such solutions.

2—The effect of the material on the photographic properties of the solution. For example, a copper tank containing a concentrated developer may show no visible corrosion after several days, but the small quantity of copper dissolved by the developer will be sufficient to produce chemical fog.

3—The time during which the solution will be in contact with the material. A japanned iron metal trough is suitable for toning baths if the solutions are removed and the trough well rinsed after use. If a developer is stored in a japanned tank, the japan will ultimately soften or peel off.

4—The cost of the material.

5—The adaptability of the material for construction purposes. Glass, for instance, is entirely unsuitable for constructing large tanks because of its fragility and the difficulty of annealing such tanks.

Materials suitable for constructing various types of photographic apparatus are as follows:

TRAYS, DISHES, AND SMALL TANKS—Since these containers are generally used for a variety of purposes, they should be resistant to all photographic solutions. Suitable materials are glass, enameled steel, hard rubber, teak wood impregnated with paraffin wax, wood coated with sheet rubber or rubberized cloth, well-glazed porcelain, or stoneware. Small tanks of Monel metal are satisfactory for washing or developing, and for fixing purposes, provided the bath is not allowed to remain in the tank for prolonged periods.

DEEP TANKS (for motion picture work and amateur finishers)—Alberene stone, slate, well-glazed stoneware, and wood (cypress) are suitable for all solutions, including toning baths. Lead-lined wooden tanks are suitable for developing and fixing baths if the joints are lead-burned. One objection to wood tanks is that they have a tendency to accumulate slime on the inside of the tank. In the case of developers containing a low percentage of alkali, tanks of portland cement have proved satisfactory.

TUBES FOR DEVELOPING MACHINES—Hard rubber, lead, type metal, and Pyrex glass[11] have given satisfaction. Lead accumulates a deposit of silver from the fixing bath, and in time this tends to obstruct the tube and it has to be removed by scraping.

TROUGHS FOR REEL DEVELOPMENT—Glazed stoneware and wood lined with sheet rubber or rubberized cloth are satisfactory for all solutions. Lead and Monel are satisfactory for developing and fixing solutions, provided the trough is emptied out after use. For acid oxidizing solutions or strong alkalies, the inside of the trough should be coated with cloth and this impregnated by applying molten hard paraffin wax with a brush, finally smoothing off the surface with a hot iron. Japanned metal ware is only satisfactory for temporary use.

METAL APPARATUS (clips, film hangers, etc.)—Monel metal is the most satisfactory material known, but it is not suitable for toning solutions. Tests made with Niaco and Rezistal steel alloys indicate that their resistivity approaches that of Monel, although no prolonged tests with actual apparatus have been made.

PIPING, PUMPS, FAUCETS, ETC.—For transporting developing and fixing solutions, lead and hard-rubber piping are satisfactory. Lead piping joints should be "wiped" or lead-burned, and not soldered. Faucets should be of hard rubber or stoneware, though Monel and type metal are satisfactory for developing and fixing solutions if continual exposure to the solution is not anticipated. Brass is not satisfactory for strongly acid fixing baths, but it is suitable with developers if the brass is first silver-plated by immersing in an exhausted fixing bath. Pumps of Monel and of phosphor bronze are satisfactory for developers and fixing baths if cleaned after use.

PRECAUTIONS TO BE TAKEN WHEN SELECTING CONSTRUCTION MATERIALS

1—Do not permit tin, copper, or alloys containing these metals to come in contact with developing solutions, especially concentrated developers, because more or less of the tin or copper will dissolve and cause chemical fog. Electrolysis caused by contact of two different metals or alloys will hasten the rate of solution of the metal and thus increase the amount of fog obtained. Soldered joints are particularly to be avoided with developers, but if such joints are unavoidable a low-tin solder or one free from tin should be used and the joints so made that a minimum of solder is exposed to the solution.

2—For fixing, toning, and acid oxidizing solutions such as acid permanganate, avoid metal whenever possible. If a metal must be used, lead is the most suitable for fixing baths, but electrolytic corrosion sets in if the joints are not lead-burned.

3—For fixing baths or strong saline solutions, avoid porous materials such as incompletely glazed earthenware, impregnated fibrous materials, or rubber compositions, because crystallization of the salts within the pores of the materials causes disintegration in a manner similar to that of ice in weathering rocks.

4—Avoid cheap rubber tubing or other materials containing free sulfur or metallic sulfides for use with developing solutions, because, as a result of the action of the alkali in the developer, soluble alkaline sulfides which cause chemical fog are formed.

ACKNOWLEDGMENT

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Pyrex Glass Plant Equipment

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CHEMICAL engineering, considered from a somewhat narrow angle, is the translation of chemical manufacturing processes from the small or laboratory scale to tonnage production in factories. Small-scale experiments are usually carried out in glass apparatus, with the result that corrosion troubles are not given much consideration until the chemical engineer is faced with the design of a small commercial plant incorporating the results of the laboratory work.

Chemical corrosion of the materials to be used in construction immediately assumes importance, as the plant equipment cannot be a mere multiplication of the laboratory apparatus. The liter flask of the laboratory has to become a still, retort, or kettle of several hundred gallons capacity, the Liebig or spiral condenser has to be changed to a design capable of handling 50 or more gallons per hour, and $^1/_4$-in. glass tubes used for connections have to be converted into 6- or 8-in. pipes. In each piece of equipment corrosion will enforce limits as to materials employed, and the final design will quite likely be a compromise of several materials, each selected with reference to corrosion conditions at certain points.

The introduction of industrial Pyrex as a plant construction material has enabled the engineer to translate, within limits, laboratory practice directly into plant equipment, and to secure the freedom from corrosion enjoyed by the research chemist. The present limits of manufacture are not final, but are capable of some further expansion, as is indicated by the progression of sizes in the past eighteen months of development work. There is, of course, a limit to the size of Pyrex articles introduced, through structural considerations, but so far the present manufacturing possibilities have not reached the safe limits set by the engineering factors of plant design.

FAMILIAR PROPERTIES OF PYREX

Pyrex glass has become familiar to most of us as laboratory ware and domestic cooking utensils. The laboratory apparatus has given proof of its resistance to heat and chemical corrosion, and the baking ware has demonstrated ruggedness under constant handling. Sudden heat shock is also a feature of most of the domestic applications, the conditions frequently being more strenuous than in plant uses. A cold pie plate put into an oven heated to 400° F. has to meet a greater thermal shock than the large evaporating dish used on a steam bath in a chemical plant.

The utilization of materials that have become familiar through use in other fields is a feature of recent chemical engineering work. As evidence there can be cited the use of Bakelite, hard rubber, stainless steel, chromium-nickel alloys, etc. Each of these has advantages as a resistant material for certain limited purposes, and finds a corresponding specific field of application. Pyrex glass, because of its resistance to most acids combined with excellent thermal properties, has a wide field of industrial use with limits set by design of parts and possibilities of manufacture.

ENGINEERING PROPERTIES OF PYREX

Before proceeding to a discussion of industrial applications, it is desirable to list briefly the various properties which have to be taken into consideration from the engineering standpoint.

Specific gravity[a]	2.25
Specific heat[a]	0.20
Elasticity coefficient[a]	6230 kg. per sq. mm.
Linear expansion coefficient[b] (19° to 350° C.)	0.0000032 per ° C.
Thermal conductivity[a]	0.0027
Dielectric strength[b]	20 kv. per 100 mil thickness
Specific inductive capacity[b]	5.75 to 5.78
Electrical resistivity (volume)[b]	10^{14} ohms
Electrical resistivity (surface)[c]	10^{14} ohms at 34 per cent humidity 5×10^8 ohms at 84 per cent humidity

[a] Corning Glass Works Laboratory.

[b] General Electric Company Laboratory.

[c] Bureau of Standards.

The chemical properties which affect design are mainly corrosion resistances at various temperatures.

The mineral acids, with the exception of hydrofluoric and phosphoric, have no appreciable action on Pyrex up to their respective boiling points. Initially, there is a very slight surface attack, the figure for constant boiling hydrochloric acid being 0.000006 g., and for fuming sulfuric 0.000002 g. per sq. cm. per hr. This initial action is succeeded by a state of practical stability.

In the case of phosphoric acid, the attack produces crystallization at the glass surface and makes accurate determinations of solubility rather difficult. An average figure arrived at by the Corning laboratories is 0.0027 g. per sq. cm. per min. Hydrofluoric acid does not attack Pyrex as readily as other glasses, this being a matter of knowledge possessed by all laboratory workers who have tried to etch beakers or flasks. The action is, however, sufficient to prevent any serious consideration of the use of Pyrex plant for hydrofluoric acid or fluoride production.

Quite recently a question was raised as to the use of Pyrex in acetic anhydride manufacture, and it was found that no measurable attack occurred in 5 hrs. at the fuming temperature.

PRESENT LIMITATIONS OF SHAPE AND SIZE

Previous mention has been made of limits imposed by present processes of manufacture. Such limits are of considerable importance to the engineer who is considering, as a preliminary stage, the use of a new material for construction work. Without this information changes in the final design may be found necessary in order to bring certain parts within the existing limits of manufacture.

Industrial Pyrex is made by various methods, the most important being pressing and blowing. Accessories for plant use, such as tees, tubulated vessels, etc., are produced in very much the same way as the smaller ordinary glass articles made by the laboratory glass blower, except that much higher temperatures are involved.

Hemispherical evaporating dishes are examples of pressed ware, the largest available size being 24 in. in diameter.

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[1] Consulting Engineer, Corning Glass Works.

More difficult shapes call for a reduction in size—drier trays, for instance, being practicable up to 12 x 18 x 3 in. Sharp angles are undesirable in pressed ware and should always be avoided.

Blowing into molds gives an externally controlled size with an opportunity to vary wall thicknesses in accordance with the use of the equipment. Parts for condensers may have a wall thickness of $^1/_{16}$ to $^1/_8$ in., whereas tower sections or large socket pipes can be made $^3/_8$ in., or even heavier. The limits of blown ware are approximately 15 gal. for necked vessels and 12-in. diameter for socket pipes.

The limits for pressed and blown articles are, of course, subject to upward revision, as the present sizes represent less than two years' development work. As an example of the enlargement of sizes, it is of interest to remember that less than a year ago a 10-liter Pyrex dish was an achievement, whereas to-day the 24-in. dish has a capacity of 30 liters.

Applications in the Industries

The growth of uses for industrial Pyrex has shown a marked increase in recent months, due no doubt to results of earlier tests with single pieces.

Generally, the industrial applications fall within four distinct classifications:

1—Uses where acid resistance is important
2—Uses where purity of product is essential
3—Uses where control is facilitated by transparency
4—Uses where resistance to thermal shock is desirable

Under Class 1 would be grouped Hart condenser tubes, S-bend nitric acid condensers, pipe lines for acid gases and liquids, acid distillation sets, and experimental towers.

Class 2 comprises such uses as pipe lines for liquid food products, evaporating and crystallizing dishes for pharmaceuticals, fine chemicals, etc., tanks for precious metal solutions, and drier trays for alkaloids, biologicals, etc.

Class 3 uses are limited but interesting: sight glasses for stills, retorts, etc., gage tubes for tanks, boilers, etc.; sight pipe sections for distilling columns; and sight pipe sections for chamber plants.

Class 4 uses merge at times into Class 1, as heat and acid resistance are often companion factors for consideration. The following applications are based largely on heat-proof qualities: receivers for hot liquids, flat pans for vacuum and atmospheric driers, and tubular condensers for organic liquids.

Methods of Construction and Use

Most of the items listed above do not involve special construction features. However, in using Pyrex equipment it is essential to remember that, while it has an extremely low coefficient of expansion, direct flame is to be avoided.

Pipe lines call for special designs if flanged joints are involved, and special cements when joints are of the socket or bell and spigot type. Flanged pipe lines cannot be made up by directly bolting two faces together, so an extra split-metal flange is used behind the Pyrex flange and kept out of direct contact by a rubber gasket. The metal flange may be cast aluminium or pressed steel. A gasket between the glass faces is desirable, and this may take the form of a silver-asbestos corrugated gasket similar to the copper automobile type, or one of the special rubberized fabrics which is resistant to the liquid or gas handled in the pipe line.

In the case of cements, it is preferable to adopt mixtures which will remain plastic in use. Hard-setting cements are liable to cause trouble through expansion. Generally, the use of a soft asbestos cord or rope filler at the base of the socket joint will be found advantageous, and with a plastic cement will give flexibility to the line.

The Effect of Velocity on the Corrosion of Steel in Sulfuric Acid[1]

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Theory

IT HAS been recognized for some time that there is a distinct difference in the processes governing the corrosion of steel under acids and under natural waters. The fundamental equation in both cases, however, as pointed out by Whitney,[2] is undoubtedly

$$\mathrm{Fe} + 2\mathrm{H}^+ \rightleftharpoons \mathrm{Fe}^{++} + 2\mathrm{H} \qquad (1)$$

The rate at which this reaction progresses is dependent on a number of factors, among which are the following: (1) metal, (2) hydrogen-ion concentration, (3) ferrous-ion concentration, and (4) removal of hydrogen.

Metal—The tendency for a pure metal to corrode is determined by its position in the electromotive series. This factor is usually of minor importance, being obscured by such effects as protective or nonprotective oxide or other films, overvoltage to the evolution of hydrogen gas, and the physical condition of the surface. In commercial steels and irons the presence of elements other than iron or of products of corrosion on the surface of the metal may materially change the overvoltage and the consequent ease of liberating gaseous hydrogen.

Acidity—Acidity is measured by the hydrogen-ion concentration of the solution, rather than by normality. For example, the hydrogen-ion concentration of 5 *N* and 2 *N* solutions of different acids is shown below.[3]

	5 *N*	2 *N*	
HNO_3	2.08	1.48	Equivalents hydrogen ion per liter
HCl	2.01	1.39	
H_2SO_4	1.84	1.01	
H_3PO_4	0.816	0.360	
HAc	0.013	0.006	

Increasing acidity increases the tendency to corrode by increasing the electromotive force for hydrogen gas evolution. The passifying action exhibited by various strong oxidizing acids is generally accredited to a rapidly formed film of adherent oxide on the metal surface, and has no direct relation to the acidity of the solution.

Ferrous-Ion Concentration—The law of mass action shows that increased ferrous-ion concentration should retard the rate of corrosion. In practice, however, the effect of other factors is so much more important that ferrous ion probably plays a minor role in the process.

Removal of Hydrogen—The rate at which hydrogen is removed is, in general, the most important factor determining the progress of corrosion. It is dependent on several important variables, and a study of this factor as affected by these variables offers the most logical method for investigating the process of corrosion in acids.

Hydrogen can be removed in two ways—by evolution of gaseous hydrogen, according to the reaction

$$2\mathrm{H} \rightleftharpoons \mathrm{H}_2, \qquad (2)$$

or by depolarization by oxidation, either by dissolved oxygen

$$2\mathrm{H} + {}^1/_2\,\mathrm{O}_2 \rightleftharpoons \mathrm{H}_2\mathrm{O} \qquad (3)$$

or by some other oxidizing agent.

The main variables are noted below under the process which they control and will be discussed in the following paragraphs.

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[1] Published as Contribution No. 79 from the Department of Chemical Engineering, M. I. T.

[2] *J. Am. Chem. Soc.*, **25** (1903), 394.

[3] Landolt-Börnstein, 5th ed., p. 1104 (from conductivity data)

Removal by Evolution of Hydrogen Gas. Hydrogen gas is evolved by an electrode reaction and is therefore dependent upon the hydrogen-ion concentration (acidity), the overvoltage, and the potential of the metal. Potential of the metal and acidity have already been discussed, and their effect can be quantitatively calculated for the case of a reversible electrode. Overvoltage, on the other hand, is a variable factor dependent upon the specific conditions. Among other things it is a function of the condition and composition of the metal surface, the rate of gas evolution, and the work done against surface tension in forming the bubbles of hydrogen.[4]

Oxidation of Hydrogen. A number of investigators[5,6,7] have shown that the rate at which iron corrodes under natural waters is largely determined by the rate at which dissolved oxygen can diffuse in to the metal surface to remove the polarizing film of hydrogen. This action of dissolved oxygen occurs in a similar manner in acid solutions, and although its effect in some cases may be overshadowed by other reactions which also remove hydrogen, it can become of predominating importance under certain circumstances. Hydrogen may be removed by other oxidizing agents, and it is highly probable that the high corrosion with dilute nitric acids is due to oxidation by the acid itself.

PREVIOUS WORK

Friend and Dennett[8] made the following experiments on the effect of velocity on the corrosion of iron in dilute sulfuric acid. A disk of pure iron foil, attached horizontally to the lower end of a vertical bronze axle and insulated by means of two rubber washers, was rotated at various speeds in a glass tank containing sulfuric acid. The amount of iron dissolved was determined by titration with permanganate.

From a consideration of the results, Friend and Dennett drew the following conclusions:

> (1) Different concentrations of acid give practically the same results at a given velocity.
>
> (2) The rate of solution is directly proportional within the error of the experiment—to the velocity of rotation. Even at 4000 revolutions, corresponding with a rim velocity of 35 miles per hour, there is no sign of falling off in the rate of solution. Evidently, therefore, the solution of iron in acid is a different process from the corrosion of iron in aerated water. In the latter case, corrosion ceases at a velocity of 3 to 5 miles per hour.

Friend also concluded that these results showed the corrosion process to be "one of solution of the metal, aided by the presence of dissolved salts."

An analysis of these results of Friend and Dennett, however, brings to light the following facts:

(1) The experiments were carried out at different temperatures, and if corrected roughly for this difference by means of the data quoted earlier in their article, the discrepancies between values at low speeds of rotation become marked.

(2) The experimental error at these low concentrations is so great that no definite conclusions can be drawn from the data obtained in this range.

(3) The range of acidity covered is very narrow.

(4) The statement that corrosion is proportional to velocity is obviously erroneous, since their straight line passes through unity and not through the origin.

The above-mentioned work was started by Friend in an endeavor to determine whether increased velocity had the same effect in acid that Heyn and Bauer[9] had observed in moving water—namely, that corrosion ceased at a very low velocity. Friend had himself subsequently noted the same effect in water,[10] although the critical velocity was 100 per cent greater. Speller and Kendall[6] and investigators in this laboratory did not check these results, but found that the corrosion increased consistently throughout the whole velocity range covered in Friend's investigations.

PRESENT INVESTIGATION

In order to gain a better insight into the mechanism of corrosion under acids, it was decided to expand the field touched by Friend and Dennett. It was further felt that a knowledge of the essential factors would be of value in dealing with the corrosion problem in commercial acid installations.

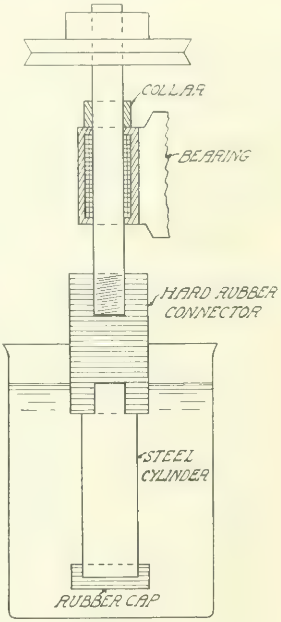

FIG. 1

The program was outlined to include a study of the effect of velocity on the corrosion of steel by sulfuric acid in strengths of from 0.005 to 5 *N* and at peripheral speeds varying from 0 to 12 ft. per sec., under atmospheres of air, nitrogen, and oxygen.

APPARATUS—The shaft shown in Fig. 1 was driven by a 1/4-h. p. motor, running at 1780 r. p. m., connection being made by means of a small leather belt. The lower end of the shaft carried the steel in the form of a cylinder approximately 0.7 in. diameter, 2.19 in. of which were exposed to the action of the acid. By varying the pulleys it was possible to obtain speeds of from 250 to 4000 r. p. m. without excessive swirling of the acid. Electrical contact between the driving shaft and the cylinder was prevented by a hard-rubber connector into which the driving shaft was screwed, the cylinder being forced into a hole in the bottom of the rubber connector drilled about 0.001 in. smaller than the head of the test piece. The rubber cap was used to prevent corrosion at the bottom of the cylinder, so that all action on the steel would be on the sides, thus giving an accurate knowledge of the velocity of the surface through the liquid.

Before inserting the cylinder in either the rubber connector or the cap, the steel was heated slightly and immersed in paraffin, which when cool made a perfect seal, preventing any acid from eating under the ends of the cylinder.

To cut down the swirling action of the liquid as much as possible, two "swirl breakers" were constructed of glass rod. These consisted of a series of U's which stood upright in the beaker and resisted the motion of the liquid.

The steel used was unannealed, and of the following analysis: C, 0.12 per cent; Mn, 0.38 per cent; P, 0.053 per cent; S, 0.034 per cent; Si, trace. A microphotograph showed this to be an excellent sample as regards uniformity and absence of segregation.

EXPERIMENTAL METHOD—Before the beginning of each run, the metal surface was smoothed by polishing with both coarse and fine emery paper, and washing thoroughly with distilled water, alcohol, and ether just before immersing the steel in the acid. To determine accurately the amount of surface exposed, the diameter of the cylinder was measured each time with a micrometer. After immersion, the speed of rotation was determined by means of a Hasler speed indicator, ten readings being taken for each run (lasting 45 min.).

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[4] MacInnes and Contieri, *J. Am. Chem. Soc.*, **41** (1919), 2013.

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[6] Speller and Kendall, THIS JOURNAL, **15** (1923), 134.

[7] Wilson, *Ibid.*, **15** (1923), 127.

[8] *J. Chem. Soc.* (*London*), **121** (1922), 41.

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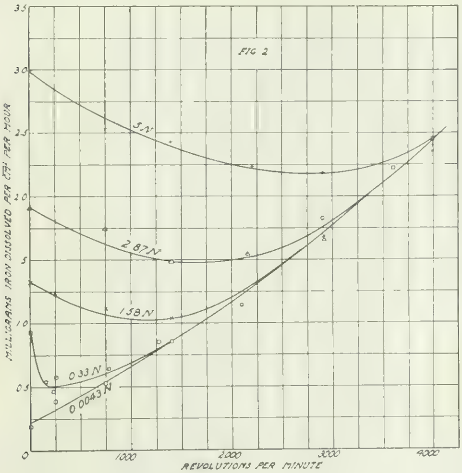
[10] Friend, "The Corrosion of Iron," Carnegie Scholarship Memoirs **11** (1922).



At the end of the run the steel was washed with water to remove any dissolved iron adhering to the shaft. The iron content of the acid was determined immediately by titration with permanganate. It is interesting to note in this connection that, while care was taken to insure complete reduction to the ferrous state either by stannous chloride or metallic zinc, it was found that titration with permanganate directly gave results almost identical with those after reduction, showing that practically all the iron was in the ferrous state, even in the oxygen runs. The temperature was kept constant at 23° C. ± 2° by immersing the beaker in a crock of water, the temperature of which was readily controlled.

In the work of Friend and Dennett,[10] the same piece of metal was used throughout to avoid as much as possible the variations in both chemical and physical properties. In this work, on account of the large amount of corrosion during the investigation and unavoidable loss on polishing, it was found impossible to use the same cylinders throughout. However, by using three pieces from the same steel bar, it was found that runs made under similar conditions gave close checks. When a run was to be made under an atmosphere of nitrogen, the acid was first boiled to expel all dissolved gases. A watch glass was then put over the containing vessels and a slow current of nitrogen bubbled through the liquid during the cooling process. During the run itself the beaker was covered with a perforated watch glass, through which the driving shaft fitted, the gas being led in over the surface at a fairly rapid rate. It was found necessary to deoxygenate the nitrogen by passing through a chain of bottles containing pyrogallol.

In oxygen runs, the gas (99.9 per cent pure) was bubbled through the acid for half an hour and the run made exactly as in the case of nitrogen.

Results—Fig. 2 gives a plot of corrosion as milligrams of iron dissolved per square centimeter per hour *vs.* revolutions per minute for sulfuric acids of varying concentration. It will be noted that the corrosion at rest varies considerably with the acidity, as follows:

Normality	Hydrogen-Ion Concentration	Corrosion at Rest
5.00	1.84	3.0
2.87	1.32	1.9
1.58	0.81	1.3
0.33	0.19	0.9
0.0043	0.0039	0.4

With the exception of the most dilute acid, corrosion decreases with increasing velocity at the start, passes through a minimum, and increases beyond that point. This minimum is realized at higher velocities for the stronger acid than for the weaker ones. It is significant that the corrosion of all these acids is the same at the maximum velocity of 4000 r. p. m.

Specimen Data Sheet

0.33 *N* H_2SO_4 under Air

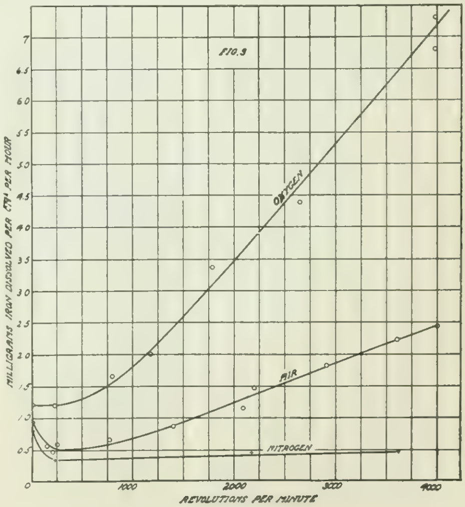
R. p. m.	Temperature ° C.	Normality of $KMnO_4$	Corrosion Mg./Sq. Cm./Hr.
0	23	0.0280	0.900
0	24.5	0.0280	0.903
0	22	0.00717	1.04
0	24	0.00717	1.03
150	24	0.0280	0.535
224	25	0.00717	0.491
225	25	0.00717	0.425
250	25	0.0280	0.618
250	24	0.0280	0.610
769	23	0.0280	0.643
765	24	0.0280	0.635
770	24	0.0280	0.634
1405	25	0.0280	0.865
1400	23	0.0280	0.846
2097	24	0.00717	1.16
2095	24	0.00717	1.11
2900	22	0.0280	1.819
2920	22	0.0280	1.825
3597	24	0.00717	2.22
3631	24	0.00717	2.23
4000	22	0.0280	2.44

Note: Zimmermann-Reinhardt method, used in runs with 0.0280 $KMnO_4$; 300 cc. H_2SO_4 used in run; 100 cc. for titration. In case of 0.00717 $KMnO_4$, reduction with Zn, 300 cc. H_2SO_4 used, made up to 500 cc. at end of run; 50-cc. sample taken for titration.

Average surface exposed to action of acid = 33.2 sq. cm

Three titrations made in each run.

Fig. 3 shows the corrosion as milligrams of iron dissolved per square centimeter per hour plotted against the revolutions per minute for 0.33 *N* sulfuric acid under atmospheres of oxygen, air, and nitrogen. Since the ordinate scale on this



plot is different from that in Fig. 2, it is convenient to note that the curve for air on this plot corresponds to the 0.33 *N* curve in Fig. 2. It will be observed that the oxygen curve shows no perceptible minimum, and that the corrosion at high velocity is far greater than that observed in any other run. The nitrogen curve is lower than the air curve and shows the same initial drop at low velocities, but is practically horizontal after reaching the minimum point. As a rough approximation, it may be stated that the average difference in corrosion, at the same velocity, between the nitrogen and oxygen curves is four times the difference between the air and nitrogen curves.

Discussion of Results

Accuracy of Data—The accuracy of the method employed can be judged by a consideration of the specimen data sheet and the experimental points on Figs. 2 and 3. The data sheet (p. 674) shows a characteristic set of values and the range of deviation between different runs. Each point is located by the average of at least two runs, which checked within 10 per cent. A series of experiments for different lengths of time show the average rate of corrosion to be 10 per cent greater in a 15-min. run than in a run of 45 min., the latter being 10 per cent greater than for a 2-hr. run. This difference is due probably to a film of carbon which is exposed as the steel corrodes and which partially protects the metal surfaces. All the experiments noted in this paper ran for 45 min. While it is probable that more interference by carbon was encountered in runs where the corrosion was considerable, the results were not seriously affected by this factor.

Two Corrosion Processes—The results indicate clearly that two processes of corrosion are proceeding in the case of aerated acids. The first process, corrosion with the evolution of hydrogen gas, occurs alone in the runs under nitrogen and will be called "Corrosion by Hydrogen Gas Evolution." The second process occurs together with the first, in runs under air or oxygen, and will be called "Corrosion by Oxygen Depolarization." Fig. 4 shows the corrosion by each process and the total corrosion for 5 *N* and 0.33 *N* acids.

Corrosion at Rest—Fig. 2 shows that the corrosion by acid at rest under air varies considerably with acidity, although the relationship between total corrosion and hydrogen-ion concentration is by no means linear. Indeed, such a relation would not be expected, since overvoltage varies with the rate of gas evolution. Fig. 3 shows that corrosion with oxygen is about 30 per cent greater than with air, while with nitrogen it is 10 per cent lower. These results mean that corrosion is occurring mainly through the process of gas evolution, and that oxygen depolarization is of secondary importance. Expressed quantitatively, the corrosion by hydrogen gas evolution is 0.8 mg. (nitrogen curve) for 0.33 *N* acid, and about 0.15 mg. by depolarization with oxygen from the air (difference between nitrogen and air curves). It is not expected that different steels would corrode at this same rate, since overvoltage, and, hence, gas evolution, is dependent upon the properties of the metal.

Corrosion at Low Velocities—At low velocities corrosion decreases, except with the most dilute acid. This is undoubtedly caused by a decrease in corrosion by gas evolution, rather than by decrease in oxygen depolarization. It will be observed that this drop holds over a greater velocity range with the stronger acids where hydrogen gas is evolved in considerable amounts. Furthermore, the nitrogen curve of Fig. 3 shows this same characteristic decrease, while it is not noticeable in the oxygen run or in the curve for 0.0043 *N* acid of Fig. 2.

Corrosion at High Velocities—At high velocities corrosion of all acids under air reaches the same value at 4000 r. p. m. This means definitely that at high velocity acid concentration is a negligible factor in the corrosion of steel by aerated acid over the acid strength in question. The runs with nitrogen, air, and oxygen prove just as definitely that oxygen depolarization is predominating in importance. At the highest velocity the relative corrosion for these three is as follows:

Nitrogen	1.0
Air	5.0
Oxygen	15.0

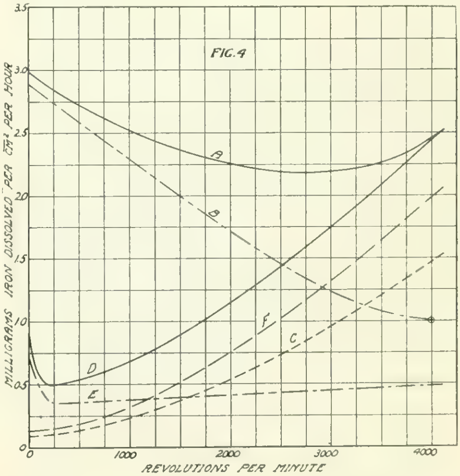
If the nitrogen run is considered to show corrosion by hydrogen gas evolution, while oxygen depolarization in the air and oxygen runs causes additive corrosion, the oxygen depolarization in the two cases will be

Air	5.0 − 1.0 = 4.0
Oxygen	15.0 − 1.0 = 14.0

The ratio of these two is 1: 3.5. It would normally be predicted that this ratio should be the same as the ratio of oxygen in the air—i. e., 1: 4.8. The discrepancy between these two ratios may be largely explained by the fact, previously noted, that a carbon residue on the steel surface cuts down the effective area of metal, and that, in runs of equal time interval, this decrease should be more marked in runs where the corrosion is greatest. Corrosion under oxygen would therefore be less in these experiments than if the surface could be maintained free from deposited carbon.

Reasons for Decreased Gas Evolution with Increased Velocity

The most logical theory yet advanced to explain the decrease in corrosion with increased velocity was suggested by MacInnes'[6] work on overvoltage.



	Curve	
	5 *N*	0.33 *N*
Total corrosion	A	D
Corrosion by hydrogen gas evolution	B	E
Corrosion by oxygen depolarization	C	F

On this plot Curves A, D, and E are experimentally determined and the points are given in Fig. 2 or 3. Curve F is obtained approximately by difference between the ordinates of D and E. Curve C parallels Curve F but is lower because corrected for increased viscosity and decreased oxygen solubility of acid. Curve B is obtained from the difference between A and C, but its lower end is independently determined by experiment; the data are shown by a cross.

From a study of hydrogen gas evolution from electrodes of platinum and other metals with very small currents, noting the location and size of the bubbles, MacInnes found among other things that:

> (1) During the process of gas evolution the overvoltage fluctuated regularly with the process of bubble formation, passing through a minimum just as the bubble disengaged from the surface; rising rapidly immediately thereafter, and passing through a maximum; diminishing as a new bubble formed and grew in size; again reaching the minimum when this new bubble disengaged.
>
> (2) The bubbles were always evolved from definite points.
>
> (3) The overvoltage was much greater at the beginning of an experiment than after bubbles had once been formed.
>
> (4) The overvoltage was less in experiments under pressure and greater in those under vacuum.

MacInnes' theory to explain these results is essentially as follows:

> Overvoltage is a phenomenon observed only when gas is evolved, and is due primarily to the energy required to form gas bubbles against surface tension. It would therefore require more overvoltage to form small bubbles than large ones, and the overvoltage would decrease as a small bubble grew in size. After a bubble had disengaged from the surface, the overvoltage would rise owing to the difficulty of starting a new bubble. From the facts that the bubbles always appeared at certain definite points, and that the overvoltage required to start the first bubble was abnormally high, MacInnes concluded that a minute gas nucleus was retained by the metal when a bubble was broken off. The absence of this nucleus at the beginning of an experiment would explain the very high overvoltage required for the formation of the first bubble. The pressure and vacuum effects were explainable on the grounds that more gas could be concentrated into a bubble under pressure for the same area of bubble surface than was the case under vacuum. As a result the overvoltage (surface tension effect) would be greater under vacuum, since more surface would be required for the same weight of gas.

Following these theories, the decrease in corrosion under nitrogen with velocity observed in this work can be explained in two ways:

> (1) Increased velocity increases the force tending to tear away bubbles, and hence decreases the size of bubbles. With smaller bubbles the work against surface tension is increased and gas evolution decreases.
>
> (2) The gas nuclei which are left on the metal after a bubble disengages are thrown off when the shaft is rotated, and corrosion decreases because of the high overvoltage required to form bubbles in the absence of nuclei.

The enormous decrease in gas evolution with velocity is clearly brought out by Curve B of Fig. 4, where corrosion under nitrogen at 4000 r. p. m. is approximately one-third of the corrosion at rest. This decrease is much more pronounced with the stronger acids and apparently all strengths of acid would evolve hydrogen at the same rate at a velocity somewhat higher than 4000 r. p. m. These results indicate that the molecular hydrogen escapes directly as a gas rather than dissolving in the solution. If the latter were true, increased velocity should increase corrosion by making it easier for dissolved hydrogen to diffuse away from the shaft.

Reasons for Increased Oxygen Depolarization with Increased Velocity

Depolarization by dissolved oxygen is fundamentally a diffusion phenomenon, controlled by the general laws governing the diffusion of energy or matter through fluid films. Dissolved oxygen in the main body of acid must diffuse through the thin film of liquid adhering to the metal surface before it can react with hydrogen at the surface, and it is the rate of this diffusion which determines the rate of depolarization. The main factors affecting diffusion in this equipment are oxygen concentration, velocity, and viscosity. The rate of diffusion should be directly proportional to oxygen concentration, a fact proved by Wilson for corrosion under natural waters. Speller and Kendall[6] demonstrated the effect of velocity and temperature on diffusion. By analogy with diffusion processes in heat transfer,[11] it can be predicted that diffusion will increase as the 0.8 power of the ratio of velocity over viscosity, and the data of Speller and Kendall check this approximation with reasonable accuracy.

The data in this paper were obtained at constant temperature, the acid was saturated with gas, and the only viscosity effect was due to differences in acids employed. The maximum velocity obtained, 4000 r. p. m., corresponds to a surface speed of 12 ft. per sec. If the oxygen effect, obtained by subtracting the nitrogen curve of Fig. 3 from the air or oxygen curve, is plotted against velocity, a fairly regular increase is observed over the whole range (Curve F, Fig. 4), although the data are not sufficiently accurate to show the exact function. It can therefore be concluded that the marked effect of oxygen depolarization is truly a diffusion phenomenon and obeys the general laws of diffusion.

It is obvious that the approximate data of Friend with weak acids, which he described as showing corrosion increasing linearly with velocity, were obtained under conditions which emphasized oxygen depolarization. Friend's conclusion, that "the solution of iron in acid is a different process from the corrosion of iron in aerated water," is true only to the extent that *in acids two processes are acting to remove hydrogen, while only one of them operates in natural water.*

Conclusions

Corrosion proceeds by the two processes of hydrogen gas evolution and depolarization by dissolved oxygen.

Corrosion at rest is primarily determined by the rate of hydrogen gas evolution, particularly with the stronger acids.

The effect of velocity is to decrease the rate of the hydrogen gas evolution. Velocity decreases the size of hydrogen bubble or throws off the gas nuclei which aid bubble formation, and hence, by increasing the work to be done in forming hydrogen, increases the overvoltage.

Velocity increases corrosion by oxygen depolarization, since it thins down the effective film through which oxygen must diffuse. At high velocities the oxygen effect becomes so predominating that acids varying five hundred fold in concentration give the same corrosion.

The net corrosion observed, being the sum of two effects, is chiefly determined by gaseous hydrogen evolution at very low velocities and by oxygen depolarization at high velocities, and passes through a minimum point in the intermediate ranges.

Acknowledgment

The writers wish to acknowledge the assistance of R. E. Wilson and D. A. MacInnes in developing the theories explaining decrease of hydrogen evolution with increased velocity.

This laboratory is at present engaged in corrosion studies of a similar nature but with a different type of apparatus in which it is planned to study oxidizing as well as nonoxidizing acids. It is hoped that the results of this investigation may be published in the near future.

[11] McAdams and Frost, This Journal, 14 (1922), 1101.

At a recent meeting of the Electric Steel Founders' Research Group, executives of the five electric steel foundries conducting coöperative research work discussed various phases of the research being done to improve the quality of steel castings and increase efficiency in methods. Formal reports were read, giving the status of present research investigations on facing sand mixtures, core sand mixtures, electric furnace practice, heat treatment of steel castings, production control, and porosity in castings, and plans were made for conducting research investigations on additional steel foundry problems.

New Applications of Phenol Resins in the Chemical and Allied Industries

By L. V. Redman

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THE phenol resins continue to find wider applications in the industries on account of their physical and chemical properties, and these applications are in the allied fields rather than directly in the chemical industry.

The most striking new application in the chemical field is the use of laminated phenol products—sold under such trade names as Bakelite-Dilecto, Bakelite-Micarta, Laminated-Redmanol, Formica, Condensite-Celeron and Fibroc—for the manufacture of octagonal plating barrels in cyanide solutions and nonconducting conveyor chains in cyanide plating. The laminated phenol products have sufficient resistance to cyanide solutions to give good life and wear in this mechanical-chemical application.

The use of the pure phenol resins as a transparent medium for measuring cylinders and conductivity cells for hydrofluoric acid is of academic interest only. The pure resins are unaffected by hydrofluoric acid solutions, and furnish transparent vessels for this use.

The laminated products made from phenol resins and woven fabrics are finding a new and extended use as pump valves and pump-valve disks in deep oil wells and in uses where corrosive animal by-products, such as slaughter-house refuse, are handled in pumps. These woven, laminated phenol-resin fabrics are also rapidly replacing other materials as silent gears in washing machines for household use and in power laundries. The material is not only silent as a gear, but it resists the dampness and corrosive effects of cleaning materials. It is replacing rawhide gears wherever rodents are a possible menace—for example, in basements, mines, etc.

These products are also used as accurate gears for vernier adjustments on radio, high-class phonograph motors, and on printing presses. Their use is also extending rapidly in the mechanical field for high-speed jigs, drills, lathes, etc., where a minimum of noise during operation is desirable.

In the automatic telephone, the laminated phenol-resin products have replaced or are replacing thin, hard rubber as the insulation used in the automatic piles, since the phenol resins when properly made have no "cold flow," and the automatic piles when locked do remain firmly locked and do not rattle after months of use, as they would do if the insulation had a cold flow. These mechanical properties of rigidity or nonflowing under pressure from bolts and screws have given the phenol resins a very extended use in the radio industry.

In the radio it is not only necessary to have accuracy of dimensions in order to give satisfactory adjustment of the instrument, but it is also necessary that these accurate adjustments be maintained—in other words, that the material from which the set is made does not creep or fall out of alignment. The phenol resins fulfil this function admirably.

In the mechanical field these new chemical products are finding extended use in automatic pencil barrels, high-grade buttons for the clothing industry, door knobs and handles, elevator dashpots, mechanical parts on typewriters and adding machines, and a multitude of other uses which need not be mentioned here.

One further interesting mechanical application that might be mentioned is the replacement of porcelain by phenol plastics wherever violent shock is liable to break porcelain, as in the discharge of high-power guns on battleships.

Laboratory Corrosion Tests

By W. S. Calcott

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THE laboratory corrosion test about to be discussed involves relatively little that is new, most of the points involved having already been brought out. It represents a combination of factors found necessary, in our experience, to obtain consistent and accurate results capable of being applied to plant design with some degree of confidence that the apparatus constructed will have the predicted life. The test evolved as the result of combining these factors has been found to give quite satisfactory results for the class of work for which it is intended—testing materials for their suitability for constructing plant and semiworks equipment.

The general method employed for determining the rate of corrosion consists in exposing the specimen to the action of the corrosive agent for a definite time and determining the loss of weight per unit area, the result obtained varying widely with slight variations in test conditions. While no published method gives sufficient detail to be used as a general method, the following method has been found to give results applicable to plant design, provided the exact plant conditions of temperature, concentration, impurities, movement of liquid, etc., are carefully taken into consideration. In establishing this test, the chief sources of variation investigated and standardized were: shape of test piece, volume of solution, temperature, time of exposure, and method of cleaning test pieces. The effect of each of these variables was separately investigated in order to permit the establishment of definite and reproducible test conditions.

The method of expressing results used, while somewhat novel, has been found to be extremely convenient from the purely practical point of view. The test is made in the usual way, the corrosion rate being found as loss of weight per unit area per unit time. In order to reduce the results to a comparable basis, however, so that data on materials of widely differing density, as, for instance, lead and aluminium, can be compared, the loss of weight is recalculated to the equivalent thickness of metal removed. The unit arbitrarily taken is inches penetration per month. This system has the further advantage that the corrosion rate itself gives an approximate idea of the probable life of a given piece of apparatus under a given set of conditions, as the thickness of metal divided by the corrosion rate gives the life of the apparatus in months. Where the metal under test pits badly, the simple loss of weight is, of course, not a fair measure of the effective rate of corrosion, as a small hole due to pitting can cause just as complete failure as a general thinning of the entire surface. In this case, the corrosion rate is estimated in this laboratory by grinding down the entire surface of the test piece until the bottom of the pits is just reached, this point being determined by microscopic examination. The combined loss of weight in the corrosion test proper, plus the loss in the subsequent grinding, is taken as the measure of the true or effective rate of corrosion.

Shape of Test Piece

The shape of test piece has already been investigated to some extent, but was reinvestigated in this laboratory for the especial purpose of determining the effect of slight variations such as may occur between different test pieces. As an edge is exposed to attack from two directions, while a plane surface is exposed from only one, the rate of corrosion should be somewhat greater in the case of the test piece with the larger ratio of edge to surface. This was verified by exposing cast-lead test strips to the action of 20 per cent hydrochloric acid at 25° C., when it was found that the rate of corrosion increased slightly (from 5.8 to 6.2 mils) as the ratio of edge to surface increased from 3 to 8.

Ratio Length of Edge Area	Corrosion In./Mo.
3.17	0.0058
3.88	0.0052
5.56	0.0055
8.52	0.0062

The effect was, however, quite small, so that a considerable variation in this factor is permissible.

Volume of Solution

Another factor obviously entering into the equation is the volume of solution as compared with the surface exposed to action. If enough metal dissolves to alter the composition of the test solution appreciably, the resulting corrosion rate may be greatly affected.

The magnitude of the affection depends on the degree of alteration of the corroding liquid, but may easily amount to 100 per cent. For instance, a lead test piece in 100 cc. of dilute acetic acid showed a corrosion rate of 0.0035 in., and in 400 cc. a rate of 0.0066 in.

Lead Dissolved in	Volume of Solution Cc.	Corrosion Rate In./Mo.
80 per cent Acetic	100	0.0035
80 per cent Acetic	200	0 0065
80 per cent Acetic	400	0.0066
98 per cent Acetic	250	0 0006
98 per cent Acetic (Satd. with $PbAc_2$)	250	0 0024
10 per cent HCl	250	0.0138
10 per cent HCl (Satd. with $PbAc_2$)	250	0.0105

For moderate rates of corrosion (less than 0.01 in.) this factor was therefore standardized at 250 cc. per test piece of 4.6 sq. in. area, as with this amount of solution the change in composition due to dissolved metal is insufficient to alter the rate of corrosion perceptibly. For higher rates an error is, of course, introduced, but in this case, as the rate would be too high to permit of plant use of the material under test, the error is for practical purposes of minor importance.

Temperature

The exact temperature of the test has also been found to be of extreme importance. Experimentally, it has been found that the effect of temperature upon the rate of solution can be expressed by the following equation within the range 20° to 100° C.:

$$\log C = A + BT$$

$$\text{or } \frac{dC}{dT} = 2.303BC, \quad \frac{dC}{dT} = KC$$

$$C = E^{A + BT}$$

$$\frac{dC}{dT} = KE^{A + BT}$$

From this, the change in the rate of corrosion with changing temperature should be an exponential function of the temperature. Our experiments indicate a change in the rate of corrosion of from 1 to 3 per cent per degree centigrade, a variation of sufficient magnitude to necessitate very accurate temperature control.

Time of Exposure

In investigating the effect of time on exposure, an unexpected result was found. The rate of corrosion, calculated to a comparable basis, was found to be a function of the time of exposure. Generally speaking, the corrosion rate calculated from a short exposure was found to be greatly in excess of that calculated from a long one. This point is illustrated by the figures obtained on mild steel in 93 per cent sulfuric acid at 22° to 27° C.

Time Hrs.	Rate In./Mo.	Time Hrs.	Rate In./Mo.
1.0	0.0308	145.0	0.0018
3.0	0.0129	216.0	0.0014
6.2	0.0103	409 0	0 0017
26.7	0.0071	727.0	0.0019
49.5	0.0032	1028.5	0.0010
91.5	0.0027		

In this case, the rate of corrosion decreased from an initial rate of 0.0308 in. to a final steady rate of 0.0015 in., a decrease of 95 per cent from the rate of the first hour and 75 per cent from that of the first 24 hrs. This high initial rate is not uniformly encountered. Aluminium in nitric acid, for instance, shows a nearly uniform rate of corrosion from the beginning. The effect is probably due to initial electrochemical surface phenomena, complicated by the slow formation, in some cases, of a protective coat. The phenomenon occurs with sufficient frequency, however, so that the results of a short test (less than 48 hrs.) are likely to be seriously in error. For accurate work it has been found advisable to run the test for two periods of 48 and 96 hrs., respectively, the difference between the two weight losses, calculated on the 48-hr. basis, being taken as the true rate of corrosion. This figure will frequently differ materially from that obtained over the short period, sometimes by several hundred per cent, and in general will be somewhat different.

Preparation of Test Piece

The method of preparing the test piece has been found to be of relatively little importance, provided tool marks and deep scratches are removed before testing. Polishing seems to be unnecessary or even disadvantageous, through altering the surface composition of the metal. The final cleansing can be done either by treating the test piece with a solvent for the corrosion product but not for the metal, or by cleaning with a mild abrasive. The second method is of more general applicability than the first.

Procedure

The test as actually used, incorporating these points, follows:

Reagents and Apparatus—*Corroding Solution.* Use 250 cc. of the corroding solution per test piece of given area (4.6 sq. in.) for fairly rapid corrosion rate (0.01 in. penetration per month). The volume should be increased in proportion for pieces of greater area.

Preparation of the Sample—*Metal Test Piece.* Size 2 x 1 x 0.1 in. (area 4.6 sq. in.). Dimensions should be accurate to 0.01 in. in order to save time of measurement and area calculated in the laboratory. Other shapes may be used within a range of ratio of length of edge to total area of test piece between 4 and 8.

Preparation. The strip of indicated size may be cut from flat sheet metal or turned from pipe. Tool marks should be removed by successive use of file and emery. Exceedingly fine finishes are unnecessary, but the surface should be clean and reasonably smooth.

Detailed Procedure—*Standard Static Corrosion Test.* Place the corroding solution in a flask or wide-mouth bottle and bring to the temperature of the test. Maintain this temperature to at least 1° C. in a carefully regulated thermostat. Suspend the test piece upon a glass hook from a stopper of such a size as to fit the flask or the bottle loosely. The stopper must be made of a material which will be unaffected by the corroding solution. Immerse the test piece in the solution when it reaches the proper temperature, closing the bottle or flask with the stopper. If the test is being made at a high temperature, a reflux condenser must be used, taking care to prevent the condensate from running directly onto the test piece.

The highest accuracy is desirable. Expose the test piece for 48 hrs. to the corroding solution. Remove from the solution, wash thoroughly in a stream of water, and remove any coating. This cleaning may be done by dissolving off the coating (lead sulfate in ammonium acetate solution, lead chloride in hot water, etc.), or by rubbing and scouring with or without a soft powder as a mild abrasive. Do not adopt any method of cleaning until the error due to its use has been determined. Weigh the test piece after thoroughly drying, especially wiping out the hole by which it was suspended on the glass hook. Immerse the test piece in the corroding solution for a second 48-hr. period. Care should be taken that while drying and making the first weight no oil or grease is allowed to get on the test piece by handling, since this would give low results. After the second 48-hr. immersion, clean and weigh again, as described above. From the loss during the last 48 hrs. calculate the average rate of corrosion (t = 48 hrs.) as indicated under "Calculations."

Run a check test simultaneously. Never place test pieces of different metals in the same container. It is permissible to place two pieces of the same metal in the same container, but they should not be in contact.

In case the metal develops pitting, this factor must be included in the results, since failure in any case will occur when a pit has entirely penetrated the metal. Determine the magnitude of this effect by grinding down on a metallographic grinding set until all the pits have just disappeared and solid metal is reached. The loss in weight during this grinding is determined and the pitting calculated as indicated.

CALCULATIONS

If W = loss in weight in grams of test piece during second 48-hr. immersion
A = area of test piece in square inches
S = density of metal in grams per cubic centimeter
t = time of exposure in hours (t = 48)
then C = rate of chemical corrosion expressed as inches penetrated per month =

$$\frac{24 \times 30 \times W}{(2.54)^3 ASt} \text{ or } 43.9\ \frac{W}{ASt}$$

In order to calculate the pitting corrosion,

let P = loss in weight in grams due to grinding out pits,
then D = rate of penetration of metal by both normal corrosion over the entire surface and local action due to pitting,

$$D = 43.9 \times \frac{W + P}{ASt}$$

The Simultaneous Combustion of Hydrogen and Carbon Monoxide[1,2]

By R. T. Haslam

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In contrast to the views of other investigators, a study of the simultaneous combustion of hydrogen and carbon monoxide shows that between 900° and 1500° C. both reactions are trimolecular:

$$2CO + O_2 = 2CO_2$$
$$2H_2 + O_2 = 2H_2O$$

The ratio of the velocity constants for these two reactions is $\frac{kH_2}{kCO} = 2.86$*, showing that hydrogen burns 2.86 times as fast as carbon monoxide.*

There is considerable evidence that the mechanism of combustion of either hydrogen or carbon monoxide alone, with or without catalytic surfaces, is different from the combustion of a mixture of these two gases in the ordinary industrial furnace where both gases are burning simultaneously.

The possibility of obtaining a lower stack loss on an overburdened gas-fired furnace or increasing production by the use of a gas with increased hydrogen content is pointed out.

PRACTICALLY all our industrial fuels—coal, producer gas, water gas, fuel oil, etc.—decompose in the course of burning to form carbon dioxide, water vapor, carbon monoxide, and hydrogen. Any hydrocarbons present in the early stages of combustion are consumed first, so that after a very brief interval the only combustible gases remaining are hydrogen and carbon monoxide.[1,*] In burning coal, for example, a combustion chamber six times the size required to burn all the hydrocarbons may be needed to consume the last traces of hydrogen and carbon monoxide.[2] The scientific design of a combustion space depends, therefore, on an exact knowledge of the combustion of carbon monoxide and hydrogen, since they are the controlling factors in designing the smallest combustion space to give a predetermined stack loss.

In view of the fact that the reactions

$$2H_2 + O_2 = 2H_2O \text{ and } 2CO + O_2 = 2CO_2$$

are industrially of the greatest importance, at first glance it seems strange that relatively little is known about them. On the other hand, when one considers the speed of these reactions, the temperature produced by the large amount of heat evolved, the marked effect of catalyzers (surfaces), and the difficulty of controlling mixing, the lack of exact data is not surprising. Owing to turbulence it is even difficult to measure the exact time the combustible gases have been burning with the oxygen. The literature indicates that little is known quantitatively of the rates of these reactions, either actual or relative to one another, and that there is serious doubt as to their order—i. e., whether bimolecular or trimolecular.

PREVIOUS INVESTIGATIONS

Falk,[3] after investigating the ignition temperatures of hydrogen, carbon monoxide, and mixtures of these gases with oxygen, states that the reaction between hydrogen and oxygen is bimolecular—i. e., one H_2 molecule reacts with one O_2 molecule, presumably to form H_2O_2, which in turn is broken down to $H_2O + O$—and that the reaction between carbon monoxide and oxygen is trimolecular ($2CO + O_2 = 2CO_2$).

Bodenstein,[4] on the other hand, measuring the reaction velocity directly, concluded that at 600° C. the combustion of hydrogen was trimolecular ($2H_2 + O_2 = 2H_2O$), and that the rate of the reaction was proportional to the ratio of surface of the container to its volume.

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[1] Presented before the Section of Gas and Fuel Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Contribution No. 33 from Department of Chemical Engineering.

[*] Numbers in text and table refer to bibliography at end of article.

Rowe,[5] on recalculating Bodenstein's work, found the results obtained could be explained as well as on the hypothesis of the reaction being bimolecular, but concluded that the instability of hydrogen peroxide at high temperatures justified considering the reaction trimolecular.

Carter[6] found that hydrogen peroxide was the first product of the combustion of hydrogen at low pressures of 80 mm. of mercury, but that no hydrogen peroxide was formed during combustion at atmospheric pressure.

Rideal,[7] catalytically oxidizing hydrogen and carbon monoxide in the presence of one another at low temperatures (100° to 400° C.), concluded that the combustion reactions were

$$H_2 + O_2 = H_2O_2 = H_2O + O \text{ and } CO + {}^1/_2\, O_2 = CO_2$$

Bone and collaborators,[8] by exploding mixtures of methane, hydrogen and oxygen and methane, carbon monoxide and oxygen, came to the conclusion that, while the "mass influence" of hydrogen was proportional to the square of its concentration, that of the carbon monoxide was in accordance with the first power. In other words, they found that the reactions were

$$2H_2 + O_2 = 2H_2O \text{ (trimolecular) and } CO + O = CO_2 \text{ (dimolecular)}$$

Bone and Haward,[9] studying the rates of explosion of hydrogen-oxygen, carbon monoxide-oxygen, and hydrogen-carbon monoxide-oxygen mixtures, found that the hydrogen-oxygen mixture on explosion reached a maximum pressure rapidly (0.005 sec.), whereas the carbon monoxide-oxygen mixtures reached the maximum pressure rather slowly (0.17 sec.). However, even small quantities of hydrogen (4 per cent by volume) accelerated the carbon monoxide-oxygen explosion rate so that the time required to reach maximum pressure approached that of pure hydrogen (0.03 sec.), the pressure-time curve bearing no similarity to that of simple carbon monoxide-oxygen mixtures. These investigators verified those of Bone, *et al.*,[8] as to the order of the combustion reactions. Bone and Wheeler,[11] studying the combustion of hydrogen and oxygen at a temperature of 450° C., showed that when the reaction was catalyzed by such surfaces as quartz, porcelain, etc., the rate of reaction was practically proportional to the partial pressure of the hydrogen.

Thus it may be seen that for the combustion of hydrogen and oxygen, Falk and Rideal consider the reaction *di*molecular, whereas Bodenstein, Rowe, Bone, *et al.*, and Bone and Haward consider it *tri*molecular. For the combustion of carbon monoxide and oxygen Rideal, Bone, *et al.*, and Bone and Haward consider the reaction *di*molecular, whereas Falk considers it *tri*molecular.

Consideration of these views indicates the strong possibility that the two combustion reactions under discussion probably act differently under varying conditions. From the standpoint of furnace design, therefore, they should be studied under conditions existing inside combustion chambers, these conditions being (1) quiet burning under approximately atmospheric pressure, (2) a temperature range of 700° to 1500° C., (3) combustion occurring in free space uncatalyzed by surfaces, and (4) both carbon monoxide and hydrogen burning simultaneously with an excess of oxygen.

METHOD

The velocity with which carbon monoxide and hydrogen burn with oxygen may be expressed as

$$-\frac{d\,CO}{dt} = k_1\,(CO)^m\,(O_2)^n \qquad (1)$$

and

$$-\frac{d}{dt}\,(H_2) = k_2\,(H_2)^r\,(O_2)^s \qquad (2)$$

The exponents *m*, *n*, *r*, and *s* are used because the orders of these reactions are uncertain. Dividing these two equations is desirable since this eliminates one variable and the necessity for knowing the time the reactions have been proceeding. Furthermore, owing to the large amount of heat evolved when hydrogen and carbon monoxide burn, it is difficult to maintain the temperature constant throughout the experiment. By dividing one reaction by the other, thereby studying the relative rate of these two reactions, the necessity for maintaining constant temperature is eliminated or minimized as long as the two reaction velocities in question change with temperature at about the same rate. That this is sound for this particular case is shown by the temperature coefficients of these two reaction rates, as determined by Falk.[3]

Temperature coefficient of reaction velocity per 10° C. rise	800° C.	900° C.	1000° C.
Hydrogen	1.31	1.13	..
Carbon monoxide	....	1.24	1.14

This leaves the general equation

$$\frac{d\,CO}{d\,H_2} = \frac{k_1}{k_2}\,\frac{(CO)^m\,(O_2)^n}{(H_2)^r\,(O_2)^s} \qquad (3)$$

which, containing so many unknowns, is unwieldy. An assumption is therefore made that $n = s$; thus canceling $(O_2)^n$ and $(O_2)^s$. This assumption is only a temporary one and will be reconsidered later. Transposing, our equation then becomes

$$\frac{d\,CO}{(CO)^m} = \frac{k_1}{k_2}\,\frac{dH_2}{(H_2)^r} \qquad (4)$$

which is only integrable with known values of *m* and *r*. The following is the integrated form, assuming $m = r = 1$:

$$\frac{\log (CO)_1 - \log (CO)_2}{\log (H_2)_1 - \log (H_2)_2} = \frac{k_1}{k_2} \qquad (5)$$

Experimentally, a stream of hydrogen, carbon monoxide, and air in excess should be burned in a long combustion chamber and the progress of combustion watched by withdrawing samples at intervals along the flue. A number of such runs should be made using relatively large excesses of air, each run with a different concentration of oxygen. If the foregoing logarithmic relationship of the disappearance of hydrogen and carbon monoxide is not a constant for the various steps in each individual run, then the assumption that $m = r = 1$ is incorrect. However, if this relationship is a constant the assumption is correct. Furthermore, if the same constant is obtained for runs with varying oxygen concentration, then our first temporary assumption is correct. Therefore, while two assumptions have been made, the validity of each may be tested separately.

Similarly, if we assume $m = r = 2$, our integrated equation is

$$\frac{1/(CO)_2 - 1/(CO)_1}{1/(H_2)_2 - 1/(H_2)_1} = \frac{k_1}{k_2}$$

and the validity of this assumption and the first temporary assumption may be tested again in a similar manner.

Table I shows various values of $\frac{k_1}{k_2}$ for different assumptions for *m* and *r* when $n = s$. Similar values of $\frac{k_1}{k_2}$ may be derived when the first temporary assumption does not hold, but when $m + 1 = s$ and $m - 1 = s$, etc.

Any values of *m*, *n*, *r*, and *s* may be chosen and the proper test derived to show their validity. Those mentioned above are, however, the most probable.

TABLE I

ASSUMPTIONS	VALUE OF $\frac{k_1}{k_2}$
$m = r = 1$	$\frac{\log (CO)_1 - \log (CO)_2}{\log (H_2)_1 - \log (H_2)_2}$
$m = r = 2$	$\frac{1/(CO)_2 - 1/(CO)_1}{1/(H_2)_2 - 1/(H_2)_1}$
$\left.\begin{matrix} m = 1 \\ r = 2 \end{matrix}\right\}$	$\frac{\log (CO)_1 - \log (CO)_2}{1/(H_2)_2 - 1/(H_2)_1}$
$\left.\begin{matrix} m = 2 \\ r = 1 \end{matrix}\right\}$	$\frac{1/(CO)_2 - 1/(CO)_1}{\log (H_2)_1 - \log (H_2)_2}$

DATA

Kreisinger, Augustine, and Ovitz[2] burned several varieties of coals under varying conditions of excess air and rate of firing, analyzing the resultant flue gases as they passed along a 40-ft. flue. Their experiments were numerous and complete, covering a wide range. After the first few feet away from the fuel bed the conditions were exactly those desired for the measurement of the relative rates of combustion of hydrogen and carbon monoxide—namely, both these gases burned simultaneously along a tube in the presence of an excess of oxygen. In the particular runs chosen for this paper the hydrogen content per 100 parts of nitrogen varied from 13.45 to 0.12, the carbon monoxide from 24.9 to 0.12, and the oxygen from 9.63 to 2.09. The temperatures of these runs ranged from 1200° to 1500° C.

In addition, a small amount of data was obtained from a similar, although shorter (10 ft.), furnace[10] fired with producer gas instead of coal, operated at temperatures from 900° to 1100° C.

DISCUSSION OF RESULTS

Table II shows the calculated ratio of $\frac{k_1}{k_2}$ for the most probable various values of m, n, r, and s.

TABLE II

	$\frac{k_1}{k_2}$ when				
RUN	$n = s$ $m = 1$ $r = 1$	$n = s$ $m = 2$ $r = 2$	$n = s$ $m = 1$ $r = 2$	$n = s$ $m = 2$ $r = 1$	$n = 2$ $s = 1$ $m = 1$ $r = 1$
Bureau of Mines.[2]					
161	1.47	0.46	0.76	0.93	2.71
134	0.88	0.35	0.72	2.74	1.53
181	1.16	0.37	0.53	1.18	3.30
180	0.89	0.30	0.41	0.66	1.76
172	0.76	0.30	0.37	0.71	1.94
193	1.69	0.45	2.94	0.99	3.89
197	0.79	0.30	0.70	0.42	1.59
199	0.72	0.29	0.76	0.52	1.12
192	3.04	0.35	0.86	1.58	4.59
177	1.02	0.34	0.51	0.74	1.92
178	1.71	0.28	0.31	0.67	5.11
195	0.90	0.34	0.91	1.59	1.47
189	0.95	0.29	0.70	0.55	2.13
Franklin, Tomlinson, and Widell.[10]					
3	0.46	0.41	0.24	0.79	0.90
4	1.07	0.39	0.56	0.76	2.04

Inspection of this table shows a uniform ratio of $\frac{k_1}{k_2}$ when $m = r = 2$ and $n = s$. All the other combinations vary considerably from run to run, thus proving the assumed values of m, n, r, and s by which these ratios were calculated to be incorrect with the exception of the particular values just mentioned. This indicates that under ordinary combustion conditions the two reactions are

$$2CO + O_2 = 2CO_2 \text{ and } 2H_2 + O_2 = 2H_2O$$

Fig. 1 shows the individual points of the various Bureau of Mines runs plotted on the assumptions proved above, that both reactions are trimolecular. The points lie very close to the straight line except at the extreme right. However, in this range a very small error in the analysis for hydrogen or carbon monoxide would throw any of these points from one side of the line to the other, making the fact remarkable that they check as well as they do.

The slope of the line in Fig. 1 gives $\frac{k_1}{k_2} = 0.35$, showing that throughout the range of temperature studied the ratio of the rate of combustion of carbon monoxide to that of hydrogen is 1 : 2.86.

A reinspection of Falk's[5] data shows that his work on the ignition temperatures of mixture of hydrogen, carbon monoxide, and oxygen also indicates that when *both* carbon monoxide and hydrogen burn simultaneously, they are both trimolecular. It will be recalled that Falk, studying each reaction separately, concluded that the combustion of hydrogen with oxygen was bimolecular, while the combustion of carbon monoxide with oxygen was trimolecular. There is the possibility, therefore, that the simultaneous combustion of hydrogen and carbon moxonide is by a different mechanism than that by which they burn separately. This view is also supported by the work of Bone and Haward.[9]

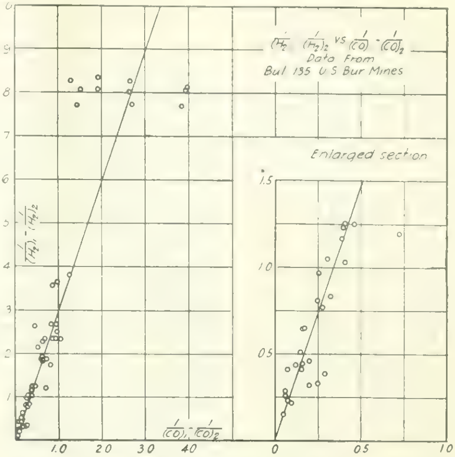

FIG. 1—SIMULTANEOUS COMBUSTION OF HYDROGEN AND CARBON MONOXIDE

IMPORTANCE

Aside from throwing further light on the simultaneous combustion of hydrogen and carbon monoxide, which brings the scientific design of furnaces a step nearer, this paper shows that under certain circumstances it is desirable to burn a gas high in hydrogen. Owing to the speed with which hydrogen burns, a gas high in hydrogen appears to be more satisfactory when the combustion chamber is too small for the task imposed, thus causing a high stack loss, or where increased output from a furnace is desired. In burning producer gas this may be attained partially by increasing the pounds of steam per pound of coal, thereby increasing the hydrogen content of the producer gas. In other cases a change to water gas or other high hydrogen gas might be desirable. Also, it seems more reasonable to attribute the beneficial results which are sometimes obtained with water gas to the rapidity with which hydrogen burns rather than to the high theoretical temperature of the hydrogen flame.

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The South African Lubricants and Chemical Works, Ltd. proposes to set up within six months an experimental plant for the treatment of oil shale from their property in Impendhle District, Natal. It is reported that this plant will have a daily capacity of 50 tons of shale, and if results are satisfactory the erection of a plant capable of treating 500 tons per day is proposed.

The Conversion of Methyl Chloride to Methanol—I[1]

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In brief, the method proposed here is to treat natural gas (methane) with chlorine under conditions conducive to a maximum yield of methyl chloride, and then by the use of lime to convert the methyl chloride to methanol. In the past, the endeavor in carrying out the chlorination of methane has been to chlorinate all the methane with the primary object of obtaining the higher chlorinated products, chloroform and carbon tetrachloride. From the work reported by the Bureau of Mines and others,[2] there is every reason to believe, however, that by using an excess of methane a product can be obtained which, while diluted with methane, will be contaminated with very little of the higher chlorinated products. The presence of this excess of methane will not interfere with the subsequent conversion of the methyl chloride to methanol. Where natural gas of suitable quality is not available, the methane can be produced catalytically from water gas, as carried out by the Cedford process.[3] At the present time methyl chloride made by the chlorination of natural gas is available on the market. This investigation, therefore, is concerned entirely with the second stage of this synthesis—that is, with the problem of the conversion of the methyl chloride to the final product, methanol.

IN NORMAL times the United States produces about one-half of the world's supply of methanol. Previous to the war this amounted to over 10,000,000 gal. a year,[4] all of which was obtained by the destructive distillation of wood, for up to the present time the so-called hardwoods have been the only industrial source of this compound. During the war the urgent demand for wood distillation products gave an impetus to this industry, which resulted in an increase in productive capacity of over 25 per cent.[5] At the present time the productive capacity of this country is approximately 17,000,000 gal. of methanol, requiring the consumption of over 2,000,000 cords of wood per year.

The yield of methanol obtained by destructive distillation amounts at best to 8 gal. per cord of wood,[2] which is less than 1.5 per cent by weight of the wood. In addition, charcoal, acetic acid, and acetone are produced. The war period, however, saw the development and establishment on a commercial scale of several competitive processes, of which acetic acid and acetone are the products. These processes are: (1) the fermentation process for acetic acid, (2) the synthetic production of acetic acid from calcium carbide, and (3) the fermentation process for acetone. Thus, with the exception of charcoal and methanol, these new processes offer competition on all the products formerly produced by wood distillation only. Moreover, developments in the metallurgy of iron and the improvements in the production of metallurgical coke have greatly reduced the demand for charcoal.[2,6] Methanol remains, therefore, the only product for the production of which the distillation of vast quantities of our most useful hardwoods is indispensable. The desirability of a synthetic method for the production of this product is accordingly evident. It is the purpose of this paper to describe such a synthetic process.

MATERIALS REQUIRED

The raw materials for methanol prepared by this process are natural gas, chlorine, and lime. Natural gas is a cheap and plentiful raw material, which has not received the chemical exploitation it deserves. Certainly, it is a far more desirable source of methanol than our valuable hardwoods. Chlorine is a raw material for which new demands are greatly needed, for the disposal of chlorine is one of the factors which has limited the growth of the electrolytic alkali industry. The electrolysis of brine produces caustic soda and chlorine in unchangeable proportions (100 lbs. sodium hydroxide to 90 lbs. chlorine). The ratio of the relative demands for these two products is very different, however, caustic soda being in greater demand than chlorine. It is the practical impossibility of the disposal of this chlorine, even as a waste material, that has prevented the increased production of electrolytic caustic to meet this relatively strong demand. By furnishing a market for chlorine this methanol process would assist in equalizing these demands and thus would be economically beneficial.

A sufficiently cheap source of methanol will assist in filling the increasing need of a new source of motor fuel. It has been shown that methanol is satisfactory for this purpose from a technical standpoint,[7] for it stands very high compression without preignition, and causes no carbon formation. These factors, together with its high vapor pressure at ordinary temperatures, make it an excellent component for a blended motor fuel.

RESUMÉ OF PREVIOUS WORK

In this investigation attention has been fixed on effecting the conversion of methyl chloride to methanol in the gaseous phase, because in this way certain advantages are gained when regarded from an engineering aspect. By this method of treatment greater continuity of operation is effected, the problem of the handling of materials is simplified, and the troubles attendant on the use of high-pressure autoclaves, necessary if the liquid phase is present, are avoided.

The reactions occurring between metallic hydroxides and alkyl chlorides in the gaseous phase have been the subject of a meager amount of investigations in the past. Dumas and Stas,[8] in an attempt to form methylene, passed methyl chloride over heated potash lime and obtained potassium formate, hydrogen, and potassium chloride. Methane was also obtained, owing, the authors state, to the decomposition of the formate. It is also shown that the presence of the formate was due to the oxidation by the potassium hydroxide of the methanol which was first formed. Sodium hydroxide was found to exert the same effect. Later Nef[9] obtained similar results on passing ethyl chloride over heated hydroxides. Using soda lime, 30 per cent of the alkyl halide was converted to ethyl alcohol and sodium acetate. Methane and hydrogen were also obtained.

In a recent paper, Whiston[10] proposed to synthesize methanol from natural gas by the chlorination of the gas and the subsequent conversion of the methyl chloride to methanol. He attempted the hydrolysis of the methyl chloride by steam, but found that no more than traces of methanol could be obtained. He also tried some experiments on calcium hydroxide as a means of effecting this conversion, and found after repeated circulation at 300°

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[1] Received December 4, 1922.

[2] *Bur. Mines, Tech. Paper* **255** (1921); Curme, U. S. Patent 1,422,838 (1922).

[3] Rideal and Taylor, "Catalysis in Theory and Practice," **1919**, p. 182.

[4] Brown, "Forest Products," **1919**, p. 221; cf. Manufacturers' Census for 1914.

[5] Tariff Information Surveys, "The Wood Chemical Industry," **1921**.

[6] Bunbury, *Chem. Age* (*London*), **6** (1922), 162.

[7] *Bur. Mines, Bulls.* **32** and **43**; *J. Soc. Chem. Ind.*, **27** (1908), 779.

[8] *Ann.*, **35** (1840), 169.

[9] *Ibid.*, **309** (1899), 126; **318** (1901), 1; *J. Am. Chem. Soc.*, **26** (1904), 1549.

[10] *J. Chem. Soc.* (*London*), **117** (1920), 183, and a private communication.

C. that the methyl chloride disappeared almost quantitatively. He determined qualitatively the presence of methanol and methyl ether in the reaction products. No experimental details or data are given. This is the first suggestion of the hydrolysis in the gaseous phase of methyl chloride to give methanol. It was, however, carried out in the absence of steam.

EXPERIMENTAL

Hydrolysis of Methyl Chloride by Means of Steam

The direct hydrolysis of methyl chloride by means of steam would obviously be the simplest and most desirable method, from a commercial viewpoint, of effecting the conversion of methyl chloride to methanol. For this reason, in spite of the negative results obtained in earlier attempts,[10] a thorough experimental investigation was made of the reaction

$$CH_3Cl + H_2O = CH_3OH + HCl$$

The methyl chloride used came in iron cylinders, each containing 10 lbs. of the liquefied gas. Its composition as determined by the methods of analysis described in a previous article[11] was found to be 99 per cent methyl chloride, the remaining 1 per cent consisting of methane and inert gas, with possibly some methylene chloride and ethylene.

The method of hydrolysis employed was to pass the methyl chloride through an apparatus very similar to that shown in Fig. 1 and described below. The gas, after leaving the meter, was mixed to the desired extent with water vapor in the humidifier, and then passed over pure silica sand in the reaction tube in the furnace. Any methanol formed was recovered by the absorption train.

From the thermal analysis of the reaction given below, it is evident that the production of methanol should be favored by high temperatures. In these experiments temperatures up to 350° C. were employed, and the ratio of water to methyl chloride was varied from 1:1 to ratios in excess of 3:1. In every case, however, the volume and analysis of the methyl chloride were practically unchanged after passing through the reaction chamber. (Absorption of methyl chloride did not exceed 1 per cent.) Traces of methanol and hydrogen chloride were produced, for their presence could be detected in the water of the absorption train.

Since these very low yields of alcohol might be attributed to a very low reaction velocity, the attempt was made to discover a catalyst to accelerate this reaction. The rare earth oxides offered hope of success in this direction, in view of their high catalytic activity in reactions involving primary alcohols.[12] Of these oxides, zirconium oxide was found by some investigators[13] to give the best results in the esterification of methanol. Since this reaction may also be regarded as an esterification reaction using a mineral acid, zirconium dioxide was tried, but it was found to have no discernible effect on the extent of the reaction. Several other substances were investigated (anhydrous calcium chloride, anhydrous aluminium chloride and silica), but none displayed any catalytic effect. At this point the search for a catalyst was abandoned, for, in view of these results and those of previous investigators, it was concluded that in all probability the equilibrium point was far over to the left side of the reaction, and that any attempt to bring about the conversion of methyl chloride to methanol in this manner must be futile. This conclusion is fully substantiated (see below) by the application of Nernst's theorem to this reaction. It may be conclusively accepted, therefore, that the direct hydrolysis of methyl chloride by means of steam cannot be employed for the commercial production of methanol.

Use of Hydroxides for Production of Methanol from Methyl Chloride

The possibility of effecting this conversion by means of metallic hydroxides was next investigated. A consideration of all the metallic hydroxides from a standpoint of cost, availability, and physical and chemical properties restricted those meriting investigation to a very few. The hydroxides of the metals below aluminium in the electromotive series were excluded from consideration on account of their instability at the temperatures required and their objectionable catalytic behavior in the presence of methanol, resulting in the decomposition of the latter.[14] Likewise, sodium and potassium hydroxides were ruled out, for it has been shown[8] that at temperatures above 200° C. they oxidize methanol to formic acid, which in turn is decomposed at higher temperatures.

Thus, there remained as the most promising hydroxides those of aluminium, calcium, and magnesium. Of these, aluminium hydroxide had an especial merit, provided it proved sufficiently stable, since aluminium chloride, formed by the reaction in view, boils at 183° C. This seemed to promise that it might be possible to accomplish the conversion of methyl chloride very effectively using this hydroxide at a temperature above 200° C., since the aluminium chloride might sublime off in the current of the excess gas as fast as it formed, thus constantly exposing a fresh surface of the hydroxide. Magnesium hydroxide, on the other hand, was least promising, for compared with calcium hydroxide it was less available and more expensive, and considerably less stable.[15]

Experiments with Aluminium Hydroxide

A series of runs was carried out to investigate the possibility of using aluminium hydroxide. The hydroxide was prepared by precipitation from a solution of aluminium nitrate by ammonium hydroxide. The precipitate was then carefully washed and dried at 110° C.

The apparatus employed was similar to that shown in Fig. 1. The hydroxide was placed in the reaction tube in the central unit of the furnace, which was carefully maintained at a uniform and constant temperature. Experiments were made using the hydroxide both *en masse* and precipitated on pumice. The methyl chloride was sent through the reaction tube, and collected in the gasometer after passing through the absorption train.

It was found possible to convert a small amount of the methyl chloride to methanol during the first few minutes of the run, but the reaction immediately ceased owing to the dissociation of the hydroxide, forming the oxide and water. Attempts were made to prevent this decomposition by using high concentrations of water vapor in the gas, but at temperatures as low as 200° C. and partial pressure of water in excess of 600 mm. it proved impossible. Hence, the use of aluminium hydroxide was abandoned.

Use of Calcium Hydroxide

Since it possessed certain advantages over magnesium hydroxide, as pointed out above, the use of calcium hydroxide as a conversion agent was next investigated.

The calcium hydroxide employed in these experiments gave the following average analysis:

	Per cent
Calcium hydroxide + trace of magnesium hydroxide	93.0
Calcium carbonate	3.0
Moisture	2.5
Impurities (SiO_2, etc.), by difference	1.5
TOTAL	100.0

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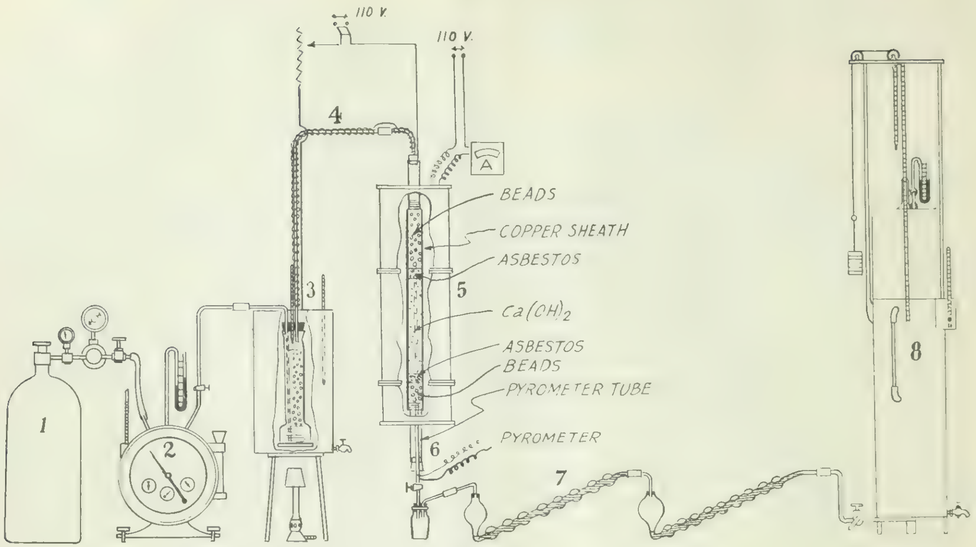


Fig. 1

The calcium hydroxide was obtained by slaking fat high-calcium lime. Five pounds of the oxide, carefully slaked, were made into a paste by adding a small excess of water, and this material was then dried in a vacuum shelf drier at 125° C. The product obtained was very uniform and fairly porous. The hydroxide was then ground and screened to sizes varying from 5 to 50 mesh. The sieving operation reduced the porosity somewhat by filling up the pores, so that the final product consisted of smooth, white, nearly spherical granules. During these experiments the analysis was checked up several times, and it was found that the composition of the hydroxide did not change.

Apparatus—The apparatus used in carrying out this experimental work is shown in Fig. 1. The gas issuing from the cylinder, 1, passes from the wet meter, 2, through the humidifier, 3, to the reaction tube, 6, in the furnace, 5, and thence through the absorption train, 7, which removes the methanol. The excess methyl chloride and any gases formed during the reaction pass on to the gasometer, where they are collected and measured. In certain experiments where dry gas was desired, a calcium chloride drying train was substituted for the humidifier.

The meter was calibrated against a standard cubic foot bottle. The water in the meter was always kept saturated with methyl chloride.

The humidifier consisted of a tower about 15 in. high by 2 in. in diameter, filled, as shown, with glass beads to within 2 in. of the top. The level of the water coincided with the height of the beads. The gas entering through a tube down the center, drawn out to a capillary opening, passed up through the beads and became saturated with vapor on its way. Any subsequent condensation of the water vapor was prevented by having the temperature of the path from the humidifier to the reaction chamber well above 100° C. This was accomplished by means of the electrically heated resistance wire, 4. The entire humidifier was immersed in a large water bath. The temperature of the humidifier did not in general vary more than ± 2° C. during a run.

The effectiveness of the humidifier was determined experimentally, and it was found that under the most extreme conditions encountered in this investigation the relative humidity of the gases after passing through the humidifier was 100 per cent.

A calcium chloride drying train (not shown in figure) was used in some of the runs to dehydrate the gas issuing from the meter. The effectiveness of this drying train was also determined and it was found that the partial pressure of water vapor in the gases issuing therefrom was approximately 2 mm. of mercury.

The reaction tube was a Pyrex glass tube of 2.5 cm. internal diameter. A heavy copper sheath surrounded that portion of the tube in the interior of the furnace. The purpose of this sheath was to equalize the temperature over the length of the tube, for without it a very considerable temperature gradient existed between the mid-point and the ends of the different units. By means of this sheath and the first and third units it was possible to maintain a temperature uniform to within ± 5° C. over a length of 25 cm. in the middle unit. This section of uniform temperature contained the charge of hydroxide (50 g.) during the runs. The first unit—which also served as a preheater—and the third unit were filled with glass beads or pure silica sand. A slit about 5 mm. wide cut lengthwise in the sheath permitted observation of the interior of the reaction tube. The furnace was placed in an almost vertical position in order to prevent the gases from channeling across the surface of the hydroxide, and, in addition, to facilitate the collection of the liquid products of reaction.

A narrow-bore Pyrex tube (2 mm. diameter) extended up the center of the reaction tube as shown, and contained a noble-metal thermocouple, by means of which the temperature was determined.

The absorption train consisted of two Meyer sulfur bulbs in series, each containing about 150 cc. of water saturated with methyl chloride. This was found by trial to be the most satisfactory type of absorption train for this purpose. Two bulbs were found to be sufficient, for the amount of methanol which was collected in a third bulb was less than the error of the subsequent analysis for methanol. Besides, it was desirable to keep the amount of water in the absorption train as small as possible in order to reduce the error due to the solution of gases therein.

The gasometer has a capacity of 20 liters, and was designed and built especially for this work. The rise of the gas holder was about 2 mm. for 50 cc. of gas, and hence volumes could be determined readily to ± 10 cc. The gas holder worked in a very narrow annulus, so the amount of liquid exposed to the gas was as small as possible. The containing fluid used was a saturated solution of calcium chloride, for it was found by trial that methyl chloride had a lower solubility in this solution than in any other available liquid.

The gasometer was carefully calibrated over the entire range of its capacity, and this calibration was then checked against the gas meter. Since the gas meter could be read to ± 10 cc. and the gasometer to ± 10 cc., the determinations of the absorption of gas taking place in the apparatus were good to ± 20 cc.

PROCEDURE—After the charge of hydroxide had been placed in the reaction tube, a blank was run to see if the apparatus was in proper working order. A few cubic centimeters of methyl chloride were permitted to flow through the apparatus in order to establish the proper pressure drop throughout the train. Readings were taken of the dial, the temperature, the meter, the gasometer, and the barometer height. The use of proper counterweights kept the pressure in the gasometer always equal to atmospheric pressure. Four or five liters of methyl chloride were then sent through the apparatus at the rate used in making the run. The meter and gasometer were then read again, and the volume of the gas sent through the meter was compared with that collected in the gasometer. A blank was not considered satisfactory unless these two volumes agreed to within 40 cc., the limit of precision of the readings. In this way any errors due to leaks or incomplete saturation of the water could be detected. In some cases blanks were also made after the runs to determine whether any such errors had arisen in the course of the run.

After a satisfactory blank had been obtained, the furnace (all three units) was brought up to the proper temperature, the gasometer emptied, and methyl chloride permitted to flow through the apparatus at the desired rate. Readings of temperatures, pressures, and volumes shown by the meter and gasometer were taken every 15 or 20 min. When it was evident that the absorption of the methyl chloride—i. e., conversion to methanol—had practically stopped, the run was discontinued and final readings were taken. (Actually, the absorption of methyl chloride did not completely stop, but reached a small constant value. See curves for Runs 1 to 9.) The duration of the runs varied from 4 to 6 hrs., and hence readings of the barometer were taken several times during the interval.

From the data thus obtained and the analysis of the initial and final products, the conversion of methyl chloride to methanol and by-products could be computed. By plotting the percentage decrease in the volume of the gas passing through the reaction tube in each 20-min. period, the course of the reaction could be followed.

DISCUSSION OF ERRORS—The precision with which the absorption of the gas could be determined was ±20 cc. Since the total gas absorbed during a run exceeded 10 liters in almost all cases, this error amounted to less than 0.5 per cent in the final calculations of yields. However, in determining the amount of gas absorbed during the 20-min. periods, it caused a very noticeable variation in the readings, which resulted in a staggering of the points on the curves. This is especially evident at the ends of the runs where the actual absorption is small. Here an error of 40 cc. amounted in some cases to approximately 30 per cent of the actual volume absorbed.

Pressure and temperature variations occurring during the run gave rise to additional errors. While the effect due to atmospheric variations was never significant, the variation in pressure of the gas in the meter, owing to pressure variations in the train of apparatus, occasionally amounted to ±2.5 mm. of mercury. This was taken care of to a great extent by using the average pressure in calculations. Fortunately, the pressure on the water of the absorption train was not subject to this change of pressure, for the pressure in the gasometer was always maintained equal to that of the atmosphere. In this way any error due to an increase or decrease in this amount of gas dissolved in the water was avoided. Variations in the temperature of the room gave rise to a more significant error, for occasionally these amounted to 2° C. The average temperature was used in making calculations. On the whole, however, the error of the determination of the total volumes of gas delivered and collected probably did not exceed 1 per cent.

RESULTS AND CALCULATIONS—The results obtained under varying conditions are shown by Curves 1 to 9, and by Table I. The data obtained in one of the runs made at 400° C., using anhydrous methyl chloride, are shown in Table II. The following example will make clear the method of obtaining these curves:

Column J is obtained by converting the readings in Column A (volume of gas admitted in cubic feet at room temperature and pressure) to gas volumes in cubic centimeters at standard conditions.

$$J = A \times 28{,}320 \times \frac{(20.95 + 0.90 - 0.61)}{30.00} \times \frac{273}{291} = A \times 26{,}880$$

since the vapor pressure of water at 18° C. = 0.61 in. of mercury

Column L is obtained similarly from Column H:

$$L = H \times \frac{29.95 - 0.61}{30.00} \times \frac{273}{291} = H \times 0.9175$$

The solid line Curve 8 was then plotted, using Column N as ordinates and Column T as abscissas

The analysis of the final products in this case was as follows

GASEOUS:	Per cent
Methyl ether	31.2
Methyl chloride	52.9
Oxygen	1.8
Methane	2.0
Hydrogen	4.8
Nitrogen	7.5
TOTAL	100.0

Methanol = 9.83 g.

Calcium chloride = 70.0 per cent = 65.4 per cent of the calcium hydroxide charged into the furnace

$$\frac{0.700 \times (74.1/111)}{1 - (0.700 \times 37/111)} \times \frac{100}{0.93} = 65.4 \text{ per cent}$$

Total methyl chloride delivered = 0.9368 × 26,800 × 0.99 = 24850 cc.

Total methyl chloride recovered = 14,260 × 0.9175 × 0.529 = 7000 cc.

Hence, total methyl chloride converted .... 17,850 cc.

Now 17,830 cc. = 17,850 ÷ 21,900 = 0.815 mol

Yield of methanol = 9.83 = $\frac{9.83}{32}$ = 0.307 mol = 37.8 per cent yield

Yield of methyl ether = $\frac{13{,}300 \times 0.312}{22{,}000}$ = 0.377 mol = 46.3 per cent yield

Yield of methane = $\frac{13{,}300 \times 0.020}{22{,}400}$ = 0.019 mol = 1.5 per cent yield

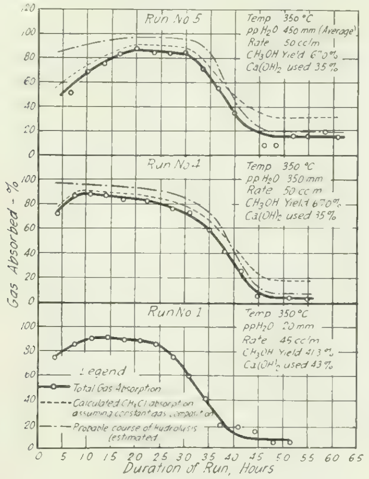
Products recovered = 0.703 mol = 85.6 per cent yield

The remainder, equal to 0.112 mol (equivalent to 1.23 liters of methyl ether), was present as methyl ether dissolved in the water of the absorption train. This was readily determined by passing a stream of methyl chloride through the train for several hours until all the ether had been swept out, and then analyzing the resulting gas mixture. The amount of methyl ether obtained was equivalent to the remainder to within 1 per cent.

The 0.815 mol. of methyl chloride used would require 0.815 × 74.1/2 = 30.2 g. of calcium hydroxide = 65.8 per cent [30.2/50 × (0.95) = 65.8] of the calcium hydroxide charged into the reaction chamber. The divergence between this and the result found by analysis is less than the error of sampling.

It is obvious that the curve drawn with the actual percentages of gas absorption as the ordinates does not give a true indication of the conversion of methyl chloride, since considerable amounts of methyl ether and some hydrogen and methane were produced, which greatly reduce the apparent absorption. This difficulty can be lessened to some extent by using the actual conversion of methyl chloride as ordinates, on the assumption that the composition of the gas received, as shown by the final analysis, was the same throughout the run. This was done and the dotted curves were obtained. This gives a closer approximation to the true conversion curves, but they are still somewhat distorted since most of the methyl ether gas generated during the run is certainly produced during the first two-thirds of the run. The actual conversion of methyl chloride to methanol and methyl ether, therefore, probably follows the course shown by the dot-dash curve.

The labor and time involved in carrying out a run from start to finish, including the necessary blanks and the analyses of all the products, were too great to permit duplicate runs to be made in every case. However, a number of duplicates were run in the preliminary investigation to determine whether the apparatus as a whole and the method followed would give reliable data. The results obtained were very satisfactory.



One instance of this is shown in Runs 1 and 2 (Table I). The analytical data for these runs are given in Table I, and it is seen that the agreement is very good. Moreover, the concordance of the results among themselves is an additional argument for the precision of the work.

As an additional check a run was made using methyl chloride prepared by Groves' method.[16] About 50 liters of the gas were collected after having been purified by passage through concentrated sulfuric acid, sodium hydroxide, and water. This gas was then displaced from the container, and passed through the meter and on through the apparatus in place of the commercial gas. The result is shown as Run 5.

The conditions of this run duplicated those of Run 4, except that the humidity was slightly higher. Here again the excellent agreement between duplicate runs is seen, and since this run was made with pure methyl chloride, it serves as a check on the entire work.

Run 7 was carried out as a continuation of Run 6, in order to investigate the small constant absorption of methyl chloride in evidence at the end of all the runs. This run was preceded and followed by a blank, and was carried out exactly as the other runs, except that the charge of calcium hydroxide was the residue from Run 6, which had not been removed from the reaction chamber. The curve obtained shows that this small constant absorption of methyl chloride continues for a considerable time.

In all these experiments a slight deposition of carbon was obtained, caused by the thermal decomposition of the methyl chloride and the products of reaction. This deposit began at the point where the entering gas first met the charge of calcium hydroxide, and during the course of the run it slowly progressed down through the hydroxide. At 350° C. it was very slight, causing the hydroxide to become gray in color. At 450° C. it caused the charge to become black. Increasing concentrations of water vapor caused a noticeable decrease in this carbon formation.

The other products obtained in these runs are shown in Table I. With the exception of a small amount of methane and hydrogen the methyl chloride was practically quantitatively converted into methanol and methyl ether. Traces of formaldehyde were also formed, but they never amounted to as much as 0.1 per cent of the methyl chloride.

THEORETICAL

The following calculated results of the theoretical relations of the reactions encountered in this investigation served as a guide in pursuing this research and as an aid in interpreting the experimental results.

THERMAL ANALYSIS OF THE PRINCIPAL REACTIONS

HYDROLYSIS OF METHYL CHLORIDE IN THE GASEOUS PHASE—

$$CH_3Cl + H_2O = HCl + CH_3OH + X_p\text{* Cal.} \qquad (a)$$

Heats of formation $-29.0 \ -58.3 = -22.0 \ -53.3 + X_p$

Therefore, $X_{p(15^\circ \text{ C.})}$ $(a) = -12.0$ Cal.

From the reaction isochor of van't Hoff,

$$\frac{d(\ln K_p)}{dT} = \frac{-Q_p}{HT^2}$$ (where Q_p = heat evolved by the reacting system),

it follows, since Q_p is negative, that the point of equilibrium will be shifted to the right as the temperature is raised, resulting in a greater yield of methanol.

CONVERSION OF METHYL CHLORIDE TO METHANOL BY MEANS OF CALCIUM HYDROXIDE—

$$2CH_3Cl + Ca(OH)_2 = CaCl_2 + 2CH_3OH + X_p \text{ Cal.} \qquad (b)$$

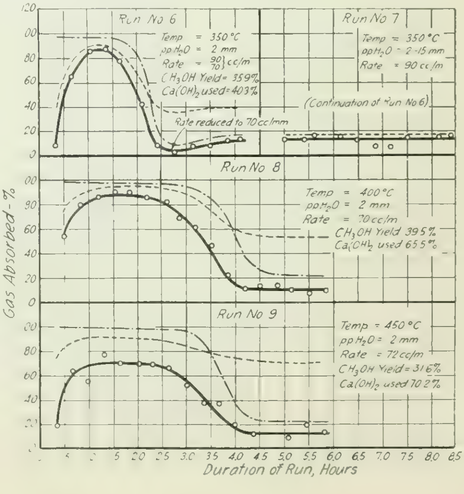
Heats of formation** $-2(29.0) - 219.1 = -173.4 - 2(53.3) + X_p$

Therefore, $X_{p(15^\circ \text{ C.})}$ $(b) = +2.9$ Cal.

Since Q_p is positive, the yield of methanol will decrease with increasing temperatures. Fortunately, the magnitude of Q_p is small so that the diplacement of the equilibrium with increasing temperature is not very great. It is possible, therefore, to obtain the advantage of the increased velocity of reaction occurring at high temperatures without any considerable diminution in the extent of the reaction.

Calculating the heat of reaction at 350° C., we have from Kirchoff's law:

$$\frac{dQ_p}{dT} = \Sigma C_p r \text{ (reactions)} - \Sigma C_p r' \text{ (resultants)}$$



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* X_p = heat of reaction at constant pressure.

** The values given, except those for calcium chloride and calcium hydroxide, correspond to the heats of formation of the compounds in the gaseous state at 15° C. from the elements.

[16] *Ann.*, **174** (1874), 377.

TABLE I—EXPERIMENTAL RESULTS

RUN	1	2	3	4	5	6	7	8	9	10
Temperature, ° C.	350	350	350	350	350	350	335	400	450	400
Rate, cc. per min	45	55	50	50	50	90	65	70	70	70
Partial pressure water, mm. Hg	20	20	180	350	425	2	300	2	2	380
Per cent CH₃OH refractive index	42.0	40.0	50.8	66.9	67.0	35.9	66.5	37.8	31.6	60.8
Per cent CaCl₂ in residue	49.5	50.0	46.3	41.5	34.8			70.0	74.0	62.6
Total CH₃Cl delivered, liters	13.70	16.99	13.85	15.28	18.12	19.15	14.20	25.10	24.80	25.92
Total gas received, liters	4.78	7.34	7.06	7.22	11.15	12.21	12.71	14.31	14.85	14.43
Per cent CH₃Cl in gas received	92.3[a]	95.0[a]	97.3[a]	79.1	78.1	66.5	95.0	52.8	36.8	69.0
Per cent CH₃.O.CH₃ in gas received				17.0	11.5	19.6	3.0	31.2	29.4	20.2
Per cent H₂ in gas received	1.6	2.0	1.0	1.1	2.1	Trace		4.8	16.0	4.0
Per cent CH₄ in gas received	0.7			0.4	0.3	Trace		2.0	9.9	2.6
Duration of run, hrs	4:45	5.00	4.30	5.00	6.00	4:05	4.00	6.10	5:30	8.00
Amount Ca(OH)₂ charged into reaction tube, grams	50	50	50	50	50	50	50	50	50	50
Volume CH₃Cl absorbed during run, liters	11.80[b]	11.83[b]	10.48[b]	9.41	9.40	11.05	2.10	18.10	19.30	15.92
Volume CH₃Cl recovered, liters	1.90[b]	5.16[b]	3.37[b]	5.87	6.72	8.10	12.10	7.00	5.50	10.00
Volume CH₄ obtained, cc.	50		. .	30	30	.	.	270	14.70	375
Per cent yield as decomposition products, H₂, CH₄, etc.	0.2	Trace	Trace	0.6	0.6			3.0	15.2	4.6
Per cent yield as CH₃.O.CH₃	58.5[a]	60.0[a]	49.2[a]	32.5	32.4	64.1	33.0	59.2	53.3	35.0
Per cent decomposition of unconverted CH₃Cl	3.0	Trace	Trace	1.0	1.0	0.5		7.0	35.0	4.2
Per cent Ca(OH)₂ converted, calculated from CH₃Cl used	....			34.2	34.2	40.3	7.6	65.8	70.2	58.0
Per cent Ca(OH)₂ converted, calculated from CaCl₂ found	43.0	43.4	40.0	35.0	34.5		. .	65.4	70.5	57.0

[a] Determined by absorption in glacial acetic acid [Allison and Meighan, THIS JOURNAL, **11** (1919), 943] Best method of analysis of methyl chloride had not yet been perfected.

[b] Calculated on basis of calcium chloride obtained.

TABLE II—CONVERSION RUN 8
(Drying Train Substituted for Humidifier)

Time	Meter Cu. Ft.	Increment Cu. Ft. (A)	Meter Pressure In. Hg (B)	Meter Temp. ° C. (C)	Furnace Temp. ° C. (D)	Gasometer Temp. ° C. (E)	Barometer In. Hg (F)	Gasometer Cc. (G)	Increment Cc. (H)	Gas Delivered Cc. (J)	Gas Received Cc. (L)	Gas Absorbed Cc. (M)	Gas Absorbed % (N)
10:50	4.1005	0.0000	+0.80	16.0	400	16.0	30.09	240	0	0	0	0	0.0
11:05	4.1230	0.0225	0.85	. .	400	....	.....	830	590	600	540	160	26.7
11:20	4.1570	0.0340	0.85		400		. . . .	1,300	470	910	430	480	52.7
11:40	4.2060	0.0490	0.85	16.0	400	16.5	.....	1,600	300	1,315	275	1,040	79.1
12:00	4.2510	0.0450	0.85		400	16.5	.....	1,800	200	1,205	185	1,020	84.70
12:20	4.2990	0.0480	0.85	16.5	400	16.5	29.96	1,960	160	1,285	145	1,140	88.7
12:42	4.3530	0.0540	0.85	16.5	404	16.5	.....	2,130	170	1,450	155	1,295	89.3
1:00	4.3970	0.0440	0.85	17.0	400		....	2,270	140	1,180	130	1,050	89.0
1:21	4.4500	0.0530	0.85		400		.	2,500	230	1,420	210	1,210	85.2
1:45	4.5150	0.0650	0.85	18.3	390		.. .	2,870	370	1,745	340	1,405	80.5
2:00	4.5500	0.0350	0.85		400	17.5	.....	3,200	330	935	305	630	67.4
2:20	4.6050	0.0550	0.85	.	400	18.0	.....	3,840	640	1,475	590	885	60.0
2:40	4.6543	0.0493	0.85		400	....	29.93	4,630	790	1,320	725	595	45.1
3:00	4.7073	0.0530	0.95	19.0	400	18.5	.....	5,850	1,220	1,420	1,120	300	21.1
3:20	4.7627	0.0554	1.00	19.0	400	....	.....	7,300	1,450	1,485	1,330	155	10.4
3:40	4.8140	0.0513	1.00	19.5	405	....	.....	8,600	1,300	1,375	1,195	180	13.1
4:00	4.8700	0.0560	1.00	19.5	405	19.0	.....	10,020	1,420	1,500	1,300	200	13.3
4:20	4.9230	0.0530	1.00	.. .	405			11,400	1,380	1,240	1,265	155	9.2
4:40	4.9795	0.0565	1.00	....	405	19.5	.....	12,950	1,550	1,515	1,420	95	6.3
5:00	5.0325	0.0530	1.00		405		.	14,350	1,400	1,120	1,285	135	9.5
5:03	5.0373	0.0048	1.00	20.3	400	20.3		14,500	150	130	135		
6 hr. 10 min.	0.9368	0.9368	0.90	18.0	400	18.0	29.95	14,260	14,260	25,105	13,310	11,800	...

whence $Q_{p(350° C.)} = Q_{p(0° C.)} + 350\ (\Sigma C_p r - \Sigma C_p r')$, where the mean specific heats are as follows:

(At 0 to 350° C.)		
	Calcium hydroxide	25.0 cal.†[17]
	Calcium chloride	19.0 cal.[17]
	Methanol	18.0 cal.[18]
	Methyl chloride	12.5 cal.[19]

† cal. = gram calories; Cal. = kilogram calories.

Hence, $X_{p\ (350° C.)}(b) = +2900$ cal. + 350(50–55) cal.
= 0.9 Cal. = 0.45 Cal. per mol methanol formed

This small heat of reaction is very advantageous in that it enables the temperature of the reaction chamber to be readily controlled.

FORMATION OF METHYL ETHER—

$$2(CH_3Cl + CH_3OH = CH_3.O.CH_3 + HCl) \qquad (c)$$
$$2HCl + Ca(OH)_2 = CaCl_2 + H_2O$$

For the purpose of this analysis we may consider them as equivalent to their sum:

$$2CH_3Cl + 2CH_3OH + Ca(OH)_2 = CaCl_2 + 2CH_3.O.CH_3 + 2H_2O \qquad (d)$$

The heat of reaction is readily computed as $Q_{p(15° C.)}$ (d) = +9.1 Cal. The same observations made concerning Reaction b apply here. (It may be noted for future reference that the heat of Reaction c = $X_{p(15° C.)}$ = −8.9 Cal.)

CONVERSION OF METHYL ETHER TO METHANOL—The authors have demonstrated that the application of the following reaction, using aluminium oxide as a catalyst, permits the conversion of the methyl ether obtained to methanol.

$$CH_3.O.CH_3 + H_2O = 2CH_3OH + X_p \qquad (e)$$
Here $X_{p(15° C.)}$ (e) = −3.1 Cal.

Evidently, increasing temperatures will favor this reaction. However, it has been shown[20] that when the reverse reaction is carried out above 350° C. side reactions occur.

APPLICATION OF NERNST'S HEAT THEOREM

In a system such as obtained here, where several reactions are occurring simultaneously, it is very difficult to interpret correctly the experimental results or to control intelligently the final products without some quantitative knowledge of the existing equilibria. To determine these by experimental means is in general a very troublesome and often an impossible task. In the present instance a knowledge of these equilibria was obtained to a surprisingly satisfactory degree by the use of Nernst's heat theorem.[21]

The application of Nernst's theorem has made it possible to calculate the free energy, and hence the point of equilibrium of any reaction occurring in a condensed system, provided the substances entering into the reaction are pure. By a further development he had extended this application to heterogenous reactions where one of the phases is gaseous. The equation for the equilibrium point which follows from his theorem is

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[17] Estimated from specific heat tables in "Tabellen zur Berchnung des gesamten und freien Wärmeinhalts fester Körper" by Miething (Halle, **1920**), pp. 31 and 35. The specific heat of calcium chloride is not given, but it is estimated from the data given for lead chloride. Lead chloride and calcium chloride have the same molecular specific heat at 0° C., and from the similarity of the compounds it is to be expected on the basis of Debye's theory that their specific heat-temperature functions will be very nearly coincident over this range.

[18] Estimated from specific heat data given in Landolt-Börnstein-Roth, "Tabellen."

[19] $C_{p(15° C.)}$ = 11.95 cal. (calculated from c_p/c_v ratio given in Landolt-Börnstein-Roth, 'Tabellen"). Using Nernst's empirical equation, $C_p = 3.5 + 1.5_n + aT$, or C_p at 350° C. = 13.0; hence, C_p (mean) (0–350° C.) = 12.5.

[20] Sabatier and Maihle, *Ann. chim. phys.*, **20** (1910), 343.

[21] Nernst, "Experimentalle und theoretische Grundlagen des neuen Wärmesatzes" (Halle, **1918**); cf. "Applications of Thermodynamics to Thermochemistry," **1907**.

$$\ln K - \frac{-Q_o}{RT} + \frac{\alpha'}{R} \ln T + \frac{\beta T}{R} + \frac{\gamma' T^2}{2R} + \ldots + \Sigma ni^{22}$$

where Q_o = heat evolved at constant pressure at absolute zero
α', β', γ' = constants depending upon the specific heats of the substances reacting
Σni = summation of constants depending upon the nature of the reacting materials existing only in the gaseous phase

In applying this theoretical equation to a specific case difficulties are immediately manifest, for it is necessary to know the specific heat as a function of temperature from absolute zero up to the temperature in question for each of the reacting materials, and in addition the same thing for the vapor pressure-temperature relations. In the present state of knowledge these are known for very few substances. In order to apply this equation, therefore, it is necessary to make many simplifying assumptions. This has been done by Nernst, among others.[23] In this work the assumptions made by him have been accepted because of the success already attained with them, and also because they have been found to give results in excellent agreement with this experimental work. On the basis of these assumptions Nernst arrives at his "approximation formula:"[24]

$$\text{Log } K = \frac{-Q_o}{4571T} + \Sigma v \; 1.75 \log T + \frac{\beta}{4.571} T + \Sigma nC$$

where Σv = the change in the number of the molecules formed by the reaction
ΣnC = the summation of the "chemical constants" of the reacting substances existing only in the gaseous phase
β = a term depending upon the specific heats of the reacting materials

Moreover, $Q_p = Q_o + \Sigma v \; 3.5T + \beta T^2$, and

$$\beta = \frac{\Sigma C_p r - \Sigma C_p r' - \Sigma v \; 3.5}{2T}$$

In order to determine the chemical constants, C, which are really the integration constants of the Clapeyron-Clausius vapor pressure equation, Nernst has used a number of devices. The results in all cases, however, are approximately the same, and are very nearly equal to the quite empirical value:

$$C = 0.14 \; \lambda/T_{B.\,P.}$$

where λ = heat of vaporization at boiling point, and T = absolute temperature of boiling point.

By the use of this formula Nernst has obtained his so-called "conventional chemical constants."[25]

While these assumptions are based on a theoretical foundation, they are by no means in strict accord with the known facts concerning the specific heat-temperature relations at low temperatures. The true chemical constants, for example, which have been calculated for a very few elements,[26] are by no means in agreement with the conventional chemical constants. Nernst advocates these assumptions simply as a set of empirical relations, which in many cases are found to give very satisfactory approximations to the true equilibrium points. The results that have been obtained by their use fully confirm this contention, at least for the cases considered.

THERMAL DATA—The successful application of Nernst's approximation formula to these reactions is possible because the substances entering into the reactions are not of great molecular complexity, so that the assumptions made by Nernst hold approximately. The thermal data employed in applying this formula are as follows:

Compound	C_p(0° C.)	λ cal.	$T_{B.\,P.}$[28]	C
H_2O	8.03[27]	9650[28]	373	3.6[28]
HCl	7.1[29]	. . . .	. . .	3.0[28]
CH_3OH	14.0[30]	8600[29]	340	3.54
CH_3Cl	11.95[31]	4870[29]	250	2.73
$(CH_3)_2O$	20.5[32]	5240[32]	249	2.95
$Ca(OH)_2$	19.6[17]	. . . .	. . .	. . .
$CaCl_2$	18.2[29]	. . . .	. . .	. . .

APPLICATION—For convenience of reference the results obtained by the application of Nernst's theorem to the reactions experimentally studied later are given here.

(1) To reaction: $CH_3Cl + H_2O = CH_3OH + HCl$ =

$$\frac{11.95 + 8.03) - (14.0 + 7.1) - 0}{2 \times 273} = \frac{-1.1}{546} = -0.002$$

Now, $Q_p = -12.0$ Cal. (Equation *a*), also $\Sigma v = 0$, since there is no volume change

$$\Sigma nC = 2.73 + 3.6 - 3.54 - 3.0 = -0.2$$

Hence, $Q_o = -12{,}000 - 0 + 0.002\,(273)^2 = -11.9$ Cal.

Substituting for log K in the equation of Nernst's approximation formula

$$\log K_p = 11{,}900/4.571T + 0 + 0.002/4.571T - 0.2$$

or $\log K_p = 2600/T - 0.00044T - 0.2$, where $K_p = \dfrac{CH_3Cl \times H_2O}{CH_3OH \times HCl}$

Therefore, at 350° C., $K_p = 5.0 \times 10^3$

Evidently, if this result is correct, it will not be possible to obtain methanol by hydrolysis of methyl chloride with steam.

(2) To reaction: $2CH_3Cl + Ca(OH)_2 = CaCl_2 + 2CH_3OH$. By a similar calculation, we obtain the following formula for this equilibrium point:

$\log K_p = -715/T - 0.0011T - 1.62$, where $K_p = (CH_3Cl/CH_3OH)^2$. Therefore, at 350° C., $K_p = 1.5 \times 10^{-4}$, or $1/\sqrt{K_p} = CH_3OH/CH_3Cl = 54$. That is, if equilibrium can be reached at 350° C., over 98 per cent of the methyl chloride can be converted to methanol.

(3) To reaction: $CH_3Cl + CH_3OH = (CH_3)_2O + HCl$. Here we have $\log K_p = -1932/T + 0.00019T - 0.3$, where, at 350° C., $K_p = \dfrac{(CH_3)_2O \times HCl}{CH_3OH + CH_3Cl} = 0.00063$.

(4) To reaction: $Ca(OH)_2 + 2CH_3Cl + 2CH_3OH = 2CH_3.O.CH_3 + 2H_2O + CaCl_2$. This reaction, as previously stated, is really the sum of two reactions. Applying Nernst's formula to this system, we have:

$$\log K_p = -2110/T - 0.0015T - 0.56.$$

Therefore, at 350°:

$$K_p = \frac{(CH_3Cl \times CH_3OH)^2}{((CH_3)_2O \times H_2O)^2} = 1.3 \times 10^{-5}$$

$$\text{Or} \quad \frac{1}{\sqrt{K_p}} = \frac{CH_3.O.CH_3 \times H_2O}{CH_3Cl \times CH_3OH} = 250 \text{ (approx.)}$$

Accordingly, this reaction will readily produce methyl ether.

(5) To reaction: $(CH_3)_2O + H_2O = 2CH_3OH$. It will be subsequently shown that this reaction furnishes a method for the conversion of methyl ether to methanol.

In this case the value $\Sigma C_p r - \Sigma C_p r'$ is so small that β is taken as zero. Then,

$$\log K_p = 678/T - 0.47, \text{ where } K_p = \frac{(CH_3OH)^2}{CH_3.O.CH_3 \times H_2O}$$

Therefore, at 350° C., $K_p = 0.25$ (approx.).

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[22] Nernst, *loc. cit.*, p. 104.

[23] *Loc. cit.*, Cederberg, "Nie thermodynamische Berechnung chemischer Affinitaten von homogenen und heterogenen Gas Reaktionen," Berlin, **1916**.

[24] *Loc. cit.*, p. 110.

[25] *Loc. cit.*, p. 111.

[26] Egerton, *Phil. Mag.*, **39** (1920), 1; Lindemann, *Ibid.*, **39** (1920), 21.

[27] From $c_p = 0.0446 + 0.0000428\,t$ (Holborn and Henning, **1905**).

[28] Same value given by Nernst, *loc. cit.*, p. 112.

[29] Calculated from data in Landolt-Börnstein-Roth, "Tabellen," p. 840.

[30] Estimated from data in Landolt-Börnstein-Roth, "Tabellen," p. 774.

[31] Calculated from c_p/c_v given in Landolt-Börnstein, "Tabellen," p. 774.

[32] Calculated from formula in Washburn, "Physical Chemistry," p. 70: $\lambda/T_{B.\,P.} = 9.5 \log_{10} T_B - 0.007T_B$.

Light Oil in Coke-Oven Gas[1]

Use of Activated Carbon in Its Determination

By Arthur L. Davis

Standard Oil Company (Indiana), Wood River, Ill.

THE quantity of the light oil in coke-oven gas, before and after scrubbing with straw oil, is generally determined by passing a definite quantity of the gas through straw oil contained in a train of bottles packed in ice, and subsequently separating the light oil from the straw oil by distillation. The removal of the light oil from the gas approaches completeness only when the flow of gas is extremely slow, and under all conditions the method of procedure is cumbersome.

The light oil present in the gas may be determined readily and accurately by the absorption of the condensable vapor in a definite quantity of gas by activated carbon, with subsequent removal by distillation of the carbon with U. S. P. cresol. Carbon of activity 40 to 50, screened 8 to 14 mesh, is suitable.

APPARATUS

The absorption requires a 0.1-cu. ft. gas meter and two activated carbon tubes complete. The carbon tubes are cylindrical containers, 1.5 in. in diameter and 12 in. in length over all, fitted with a 20-mesh screen in one end, with 1-in. breasts and screw caps on both ends. Four connecting caps consisting of 1-in. screw caps carrying $^5/_{16}$ x $^3/_4$-in. copper tubes soldered in the centers and fitted with $^1/_{16}$-in. rubber gaskets are used on each carbon tube during the absorption proper.

The distillation of the enriched activated carbon with cresol to remove the light oil is made using a 500-cc., round-bottom, side-neck, Pyrex distilling flask; a 4-in. ring burner; a 200° C. thermometer; a "Barrett standard" condenser; a 200-cc. separatory funnel graduated to 100 cc.; U. S. P. cresol; and sodium hydroxide solution of specific gravity 1.10 to 1.15.

PROCEDURE

ABSORPTION—Place 300 cc. of activated carbon in each of the two carbon tubes. Screw a connecting cap with rubber gasket to each end of each tube, and tighten with a pair of combination pliers.

Connect the inlet of the wet gas meter to the gas sampling tube and allow gas to pass through for several minutes to insure a thorough displacement of air. Turn off the gas, set the indicating hands of the meter to the zero position. (*Caution:* See that the hands are reasonably loose before turning so that the driving shafts will not be twisted.) Connect the top of the first carbon tube to the outlet of the gas meter, the bottom of the first tube to the bottom of the second tube, and either allow the residual gas coming from the top of the second tube to escape or be conducted away by an attached exit tube. *Keep the tubes in a vertical position.*

Pass an amount of gas containing approximately 30 to 40 cc. of light oil through the absorption tubes, at the rate of 10 to 15 cu. ft. per hr. At the completion of the absorption note the volume of gas passed, the temperature of the gas, and the barometric pressure.

DISTILLATION—Place the enriched carbon from the first tube in a 500-cc., side-neck, Pyrex distilling flask, add 125 cc. of cresol, *mix thoroughly by shaking in the flask*, insert the thermometer in neck of the flask, and connect to a "Barrett standard" condenser. Heat carefully with the ring burner and distil at a moderate rate till the temperature of 180° C. is reached. Collect the distillate in the 200-cc. separatory funnel, which is graduated to 100 cc. Add 125 cc. of sodium hydroxide solution, specific gravity 1.10 to 1.15 (8 to 13 per cent), and agitate thoroughly. Care should be taken to release the pressure of the gas which is often built up. Allow to stand for a few minutes, run off the sodium hydroxide solution, and record the volume of light oil obtained.

Repeat the foregoing procedure with the second carbon tube. Record the volume of light oil obtained separately.

The sum of the two volumes of light oil obtained above gives the total volume of light oil from the volume of gas passed at the temperature and barometric pressure recorded.

CALCULATION—The amount of light oil present in the gas (volume corrected to 15.5° C. (760 mm.)) is calculated as follows:

$$\text{Total volume of light oil} \times 0.264 = \frac{\text{Gal. light oil per}}{\text{1000 cu. ft. gas}}$$

$$\text{Cu. ft. gas} \times \frac{288.5}{273 + \text{temp. °C.}} \times \frac{\text{Bar. press.}}{760}$$

Gal. light oil per 1000 cu. ft. × 12 = Gal. light oil per ton of coal

(One ton of coal produces approximately 12,000 cu. ft. of gas)

VOLUME OF GAS REQUIRED

In order that the time required for making an absorption may be fairly accurately determined before making a test, the volume of gas containing a certain amount of condensable vapor should be known. The volume of gas containing approximately 30 to 40 cc. of light oil is shown in the table.

VOLUME OF COKE-OVEN GAS REQUIRED FOR CHARCOAL ABSORPTION METHOD

Gal. Light Oil per Ton Coal (12,000 Cu. Ft.)	Cu. Ft. Gas Required for Determination
0.5	190–250
1.0	95–125
1.5	63–83
2.0	47–60
2.5	38–50
3.0	31–41
3.5	27–36
4.0	24–31
4.5	21–28

In making routine analysis by this method it is advised that the determination of the gas entering the scrubbers and the gas leaving the scrubbers be made simultaneously.

The spent activated carbon containing cresol may be revivified, but it is more satisfactory to use fresh material for each determination.

Fall Meeting of American Electrochemical Society

The next meeting of the American Electrochemical Society is to be held in Dayton, Ohio, September 27, 28, and 29, 1923. The meeting will include a symposium on electrochemistry of gaseous conduction, in charge of Duncan MacRae, Research Laboratory, Westinghouse Lamp Co., Bloomfield, N. J., and a symposium on recent progress in electrolytic refining, under the chairmanship of F. R. Pyne, U. S. Metals Refining Co., Carteret, N. J. An innovation at the meeting will consist of round-table discussions on electric-furnace brass-foundry practice, organic electrochemistry, chlorine, and electroplating. There will also be excursions to local plants.

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[1] Received August 12, 1922.

Sulfo-Acid Bodies in Lubricating Oils[1]

By **G. L. Oliensis**

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In "coking" lubricating oils in agitators, or in premature neutralizing, some sulfo-acid bodies, etc., are reincorporated into the oil from sludge. Breaking resultant emulsion or blowing bright merely causes some of these to go into perfect solution in oil. The Conradson demulsibility test and the Vacuum steam test cause these bodies to be thrown out as a soapy layer below the oil, and therefore constitute qualitative tests for these bodies, this soapy layer being sometimes foamy, sometimes thick and homogeneous. The Vacuum Company regards as slop only the thick, soapy layer, but experiments indicate the foamy layer to be slop in less concentrated form.

Evidence is cited that this layer consists of sulfo-acid bodies, etc., and that the presence of slop indicates imperfect treating. A discussion as to whether or not its presence is harmful, and the usefulness of the Conradson test in this connection follows.

ONE of the most complicated solubility problems that the oil chemist has on his hands is that involved in treating petroleum oil with sulfuric acid. Roughly speaking, the action of the sulfuric acid is a very simple one—namely, it precipitates from the oil certain tarry and gummy bodies which it renders insoluble in that medium, and settles with these bodies to the bottom of the agitators in the form of sludge, which is then drawn off, leaving the oil free of all impurities. Actually, however, the action of sulfuric acid is far more complicated and far less clear-cut, and the possibilities of intersolubility among the many reaction bodies formed are well-nigh infinite, as will be observed from the following brief summary of the more important of the many reactions involved:

1—The diolefins and similar unstable hydrocarbons in petroleum oil are, generally speaking, carried down by the sulfuric acid as an insoluble sludge. However, such portions of the sludge as remain in the oil, either through adherence to the agitator lining or through incomplete separation, are often in large part reincorporated into the oil in emulsified form during coking, and after neutralization become soluble therein, existing probably as oil-soluble colloids, which recent investigations have indicated are so favorable to emulsions of the water-in-oil type.

2—The mono-olefins and aromatic hydrocarbons, when treated with concentrated sulfuric acid, form with the latter very complicated and generally unstable alkyl sulfuric acids and esters of that acid, many of which are soluble in the upper oil layer and remain there, whereas a portion is soluble in the acid sludge and is carried down into the latter. These bodies, during coking and subsequent neutralization, are probably modified considerably in their solubility tendencies; but it is safe to assume that at least a large portion of them is retained in the oil to the end, in the form of more or less unstable neutral esters of sulfuric acid and alkyl sulfates which may be soluble both in oil and in water.

3—Aromatic and other hydrocarbons, in presence of fuming acid, form (*a*) sulfonic acids, which after neutralization are converted into water-soluble sulfonates, and (*b*) the so-called naphthenic acids, which are soluble in oil in their acid state, and in water when neutralized to naphthenates. These sulfonates and naphthenates are genuine water-soluble soaps of unique properties, though their bearing here will be limited to their tendency to form oil-in-water emulsions.

It will thus be seen that by the time it has been coked and neutralized, the oil, so far from being clear of all unsaturated and tarry bodies, may contain a formidable collection of all kinds of oil-soluble and water-soluble colloids, soaps, and other compounds, much of which, being of a nature calculated to develop oil-in-water and water-in-oil emulsions, helps to reincorporate into the oil any sludge bodies present in mechanical suspension, and thus still further aggravates the emulsion-forming properties of the oil, as described under (1) above.

The result is that when the treater has reached the stage of washing the neutralized oil, he is often confronted by obstinate emulsions that baffle his efforts. In milder cases of emulsion, of course, he could resort to agitation by steam, or even by settling at slightly elevated temperatures, but in these more refractory emulsions such treatment would be totally inadequate. It has been found, however, that the addition of a small amount of a water-soluble soap and agitation with steam will often successfully break the most persistent emulsions; and it is significant that a water-soluble soap rather than an oil-soluble ingredient has to be used, because it indicates that the bodies responsible for the obstinate emulsions in those cases must have been essentially of the opposite type—namely, oil-soluble emulsifying agents, such as neutralized sludge bodies.

After an emulsion has thus been broken, the oil is by no means entirely free of the hydrocarbon bodies that were first responsible for it. The oil still shows a more or less pronounced haze, due to the presence of water which is held there in the water-in-oil phase by the emulsion-forming bodies still retained. To get rid of this haze, the treater usually blows the oil with air at a slightly elevated temperature. The function of this blowing is purely mechanical; it helps carry the water globules out of the oil in the jet of air, and it would be possible to render an oil bright by merely heating it at some temperature below the boiling point of water till the moisture has volatilized; but the emulsion-forming bodies are not removed at the same time, and have only entered into genuine solution, or colloidal solution, through the dehydration process involved in blowing the oil bright.

These foreign bodies exist in very small amounts in the finished oil, and it is therefore practically impossible by chemical tests to identify them accurately in their manifold manifestations. Fortunately, however, advantage can be taken of an interesting reaction which takes place when such an oil is agitated with steam in the presence of water and then allowed to settle. The steam seems to bring down these colloidal emulsion-forming bodies in the form of either a creamy or foam-like layer which collects between the oil layer above and the water layer beneath.

The usefulness of this reaction has been recognized in two current demulsibility tests, developed, as far as we know, independently of one another. One is known as the "Vacuum Steam Test," and the other as the "Conradson Demulsibility Test," which is fully described in past literature.

VACUUM STEAM TEST

The Vacuum steam test is rather crude. It consists of placing about 2 in. of water in a pint or quart milk bottle, adding 1 in. or so of oil and agitating with open steam. The mixture is then allowed to stand aside for about one-half hour and the appearance of the emulsified layer, if any, between the oil and water noted. If there is no emulsified layer or the layer is of a foamy, bubbly character, the oil is supposed to be of good quality. If, however, the emulsified layer is thick, creamy, and homogeneous in appearance, it is called "slop" (which is understood, in a general way, to be due to traces of sludge retained in the oil through inefficient treating) and the oil is adversely reported upon. The rapidity of separation of the layers is not especially noted. This steam test, though crude, is the only demulsibility test which judges quality by the appearance of the emulsified layer.

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[1] Presented before the Division of Petroleum Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

Conradson Test

The Conradson test is far more precise in its provisions, but basically is the same. It consists in placing 100 cc. of the oil to be treated and 20 cc. of distilled water in a 200-cc. graduated cylinder and agitating with open steam for 10 min. The graduated cylinder is then placed in a water bath maintained at 130° F. and the respective appearance and volume of the oil, emulsion, and water layers are observed from time to time for 1 hr.; but the actual demulsibility figure is obtained, not from the speed of separation or the appearance of the three layers but from the percentage of water retained in the oil layer at the end of the hour, the difference between 100 and the per cent of moisture giving the demulsibility figure.

The Conradson method has not been used very much in the trade and is not very well known, nor has it yet received official recognition. The American Society for Testing Materials, which has been engaged recently in developing a demulsibility test, has made a rather keen thrust at the Conradson test in its report, to the effect that there is no favorable comment to be found anywhere in current literature relative to the Conradson method except that of Mr. Conradson himself. The writer, however, after several years' experimentation with the method, has found that it is capable of precision, and can give concordant results repeatedly in the hands of different operators. In fact, the generous amount of oil one begins with, and the comparatively large height occupied by the columns of oil, emulsion, and water in the cylinder, make it possible to take quicker and far more accurate readings than by any other method; moreover, the size of the receptacle, the proportion of water to oil, and the manipulation prescribed (which, by the way, is exceedingly simple) seem to bring out inter-reactions between the oil and water which in other emulsification tests (such as the Navy and the R. E. method of the A. S. T. M.) either fail to appear at all or are difficult to observe and measure; yet which, when present, can throw an interesting light on the *quality and purity of the oil*, quite apart from its demulsifying powers.

To bring out this twofold utility of the Conradson method, the test is conducted precisely as originally proposed by Conradson, but the method of reporting is modified as follows:

(*a*) The volume of the three layers that separate out after emulsification is noted and recorded at the end of each of the first 5 min., and at the end of 10, 30, and 60 min. These data give very accurately the speed of demulsibility.

(*b*) The appearance of the three layers is also noted, and will serve to indicate the quality and purity of the oil.

Interpretation of Data Obtained

Differences in Texture of the Emulsified Layer—The Vacuum steam test bases its classification of oils upon the texture of the emulsified layer—a light, foam-like texture having no special significance and casting no reflection on the quality of the oil tested, while a thick, creamy, and homogeneous texture indicates poor refining. The Vacuum Company, therefore, seems to regard this difference in texture as a difference in kind. The author has found, however, that this difference is not so much in kind as in degree, and that a light, foamy emulsion layer is caused by the presence in the oil of a much smaller amount of slop or emulsion-forming bodies than is found in oil yielding a heavy, creamy emulsified layer.

This can be demonstrated in a number of ways: (*a*) by introducing into an oil, A, of very rapid demulsibility and no emulsified layer, a small amount of oil, B, which yields a pronounced slop; or (*b*) introducing into oil A a small amount of the isolated slop from oil B; and then running a Conradson demulsibility test on such mixtures.

If the slop were a definite compound that was thrown out of the oil by the steam, it could reasonably be expected that in the two experiments cited an emulsified layer would be formed of the same creamy texture as oil B itself yielded, only in a volume proportionately smaller. Such, however, was not the case. The emulsified layer in the two mixtures came down light and foam-like in texture, growing denser and finer, or lighter and more open, according as the amount of oil B in A was increased or diminished.

Unfortunately, it cannot be assumed that the amount of emulsified layer is in all cases proportionate to the content of emulsion-forming bodies in an oil. This is because the rapidity of the breakdown of the bubbles formed during emulsification depends not only on the freedom of the oil from such bodies, such as soaps, oil-soluble colloids, etc., but also on the comparatively low viscosity of the material tested. Should the oil have a high viscosity, that feature would in itself retard the breakdown of the emulsion, even though entirely free of impurities.

The question then arises—when an oil of comparatively high viscosity shows an emulsified layer, how can one decide whether it is due solely to the increased body of the oil or to impurities present? This point can be settled either by diluting with a lighter viscosity oil of perfect demulsibility to a standard viscosity (and for that purpose 200 viscosity at 100 suggests itself as most appropriate), or by repeating the demulsibility test on the same sample of oil. If the emulsified layer is due to emulsion-forming bodies present in the oil, these will be largely removed by the first steaming, and a second steaming of the same sample will show a marked reduction in the volume of the emulsion layer and in the time of separation; whereas if the layer is due merely to high viscosity, repeated steaming will not materially reduce the volume of the emulsified layer or the time of separation.

Position with Respect to Oil and Water Layers—So far, we have been dealing with the appearance and volume of the emulsified layer. Still more interesting information is obtainable from its position with respect to the oil and water layers.

As already indicated, the various impurities existing in a treated and finished oil may be roughly divided into two classes. The predominant and most frequently occurring class consists of bituminous colloids derived from the tarry matter in the sludge or otherwise, which are oil-soluble in nature; hence, tending to form water-in-oil emulsions in the presence of water. Besides these, the oil frequently contains traces of water-soluble bodies, such as soda soap, sodium sulfonates, etc., which tend to form, not water-in-oil, but oil-in-water, emulsions in the presence of water. According to whether the one or the other class of emulsifying agents is present or predominant in the oil, the latter yields, under the Conradson steam test, a differently "placed" or "built-up" emulsified layer.

In the presence of oil-soluble colloids there is a sharp line of demarcation between the upper surface of the emulsified layer and the oil above it, while the lower surface is wavy, uneven, and indefinite. The emulsified layer, furthermore, is densest at its upper level and grows lighter and more open at its lower level, the whole layer appearing to extend downward from the oil stratum into the water stratum. This kind of emulsion is of the water-in-oil phase, as is to be expected when the emulsifying agent is of the oil-soluble type.

When water-soluble emulsifying agents are present, the exact reverse takes place. The sharp line of demarcation now appears between the lower surface of the emulsified layer and the water beneath it, while the upper surface is irregular and indefinite. Furthermore, the emulsified stratum is densest at its lower level and grows more open in texture at the upper, the entire emulsified stratum appearing to extend upward from the water into the oil stratum. This kind of emulsion is of the oil-in-water phase, since it is produced by a water-soluble emulsifier. Oils containing such water-soluble soaps, even in exceedingly minute amounts, froth and lather excessively during steaming, and may even run over the rim of the cylinder if great care is not taken.

In less frequent cases, where both classes of emulsifying agents are present, both the oil-in-water and water-in-oil phases may be encountered in the same emulsified layer. In such cases there is no sharp line of demarcation between the emulsified layer and either the oil above or water below. Instead, it exists as a band which appears densest at its center, and extends unevenly and with diminishing density both upward into the oil and downward into the water stratum.

These phenomena may be conveniently demonstrated by incorporating into a perfect demulsibility oil small percentages of (*a*) neutralized sludge or calcium soaps, (*b*) water-soluble sodium soaps, or (*c*) combinations thereof, and studying the behavior of these mixtures under the Conradson demulsibility test. The steamed mixtures may even be allowed to cool and then shaken by hand, and as in that way the individual bubbles move more slowly and are of far larger size than under vigorous steaming, it is possible to watch with the naked eye the gradual accretion of the mass of bubbles into an emulsified layer and its subsequent breakdown on standing; this is indeed an interesting and absorbing study, as it reveals more strikingly than anything else the essential difference in the behavior of an oil-in-water and a water-in-oil phase of emulsion, and makes it clear why the two, when building up between the oil and water strata, should assume the form they actually do, as described in the three preceding paragraphs.

It can thus be seen that from the relative position of the emulsified layer can be deduced the character of the impurities present in the oil—particularly whether of an oil-soluble class, such as neutralized sludge and tar bodies, or of the water-soluble class, such as sodium soaps; and from the texture and density as well as volume of that layer, a roughly quantitative estimate may even be made of the amount of such impurities. Further work along these lines is now being done, which it is hoped will enable us to amplify the foregoing observations.

Significance of Test

The question now naturally arises—what is the real significance of all such information as this, as far as the actual quality of the oil is concerned?

More specifically, it is contended that a demulsibility test would serve admirably in ascertaining the suitability of a turbine oil or a marine engine oil, as both of these oils are in continuous contact with steam or water; yet, the promptest separation is essential in the former while the most stable emulsification is desirable in the latter. But inasmuch as the greater part of lubricating oil production of present-day refineries consists of motor oil, which normally does not come in contact with water at all, why worry about the demulsibility test? The appropriate answer to this question may be gathered from what has been submitted earlier in this paper—namely, that it is quite true the speed of demulsification is not a factor of primary importance in internal-combustion engines; but the demulsibility test also yields information having to do with the quality of the oil and its freedom from impurities, a matter evidently entirely apart from its demulsification tendency, and such additional information *is* of undoubted importance whether the oil normally comes in contact with water or not.

But even so, it may be argued, inasmuch as the content of impurities, whether oil-soluble or water-soluble, is admittedly very small, how can we prove, even if these were deleterious to the oil in large amounts, that the small traces actually present could affect the oil to any noticeable extent? Finally, bearing in mind that many of the lubricants in high standing in the market are intentionally blended with fatty oils and soaps to impart certain desirable qualities to them, how can we tell but that these foreign ingredients revealed in the oil by the Conradson test do actually increase its lubricating value, efficiency, and durability?

It is indeed difficult to answer these questions with assurance. However, even conceding for the sake of argument that the foreign bodies referred to do benefit the oil, or are perfectly harmless, a chemist has a right to know, and the plant management should want to know, whether a particular oil has been carefully refined and cleaned, and the Conradson test will give him information on that point.

However, who will say that these complex bodies under discussion do not hurt the oil? No one can deny that there has been considerable conjecturing in lubricating circles as to the causes of certain well-known breakdown phenomena in oils under service. Many hypotheses have been advanced to explain why some oils last so much longer than others, why some oils seem to deposit much carbon and others do not, and why, in fact, the production from the same refiner makes a brilliant service record one time and fails dismally the next. These hypotheses are gradually crystallizing into two distinct theories—namely, the "cracking" theory and the "oxidation" theory. According to the former the oil is cracked by the exceedingly high temperatures to which it is subjected in the cylinders, and carbonizing sets in as a result. The "oxidization" theory is that actual cracking does not take place to any large extent, but that the oil, being at all times in contact with the air, will, at the moderately high temperatures to which the oil is exposed in service, oxidize to form tarry, insoluble bodies which eventually carbonize; and that the presence of sludge or other tarry impurities in the oil, or contact with the surfaces or dust of certain metal catalysts, will considerably aggravate this oxidization tendency.

The writer is inclined to believe that there is a certain amount of truth in both theories, and that the disintegration of oil is due in part to cracking and in part to oxidation. When we bear in mind the tremendous heat generated at the point of explosion in the combustion chamber, it is easy to see that cracking can undoubtedly take place through oil working past the piston rings into this cracking zone, and after partial carbonization dribbling back on the return stroke to the main body of the oil. Furthermore, if this may be expected of a perfectly refined petroleum oil, cracking of a much more aggravated form can be anticipated when the oil contains the notoriously unstable sulfuric esters and alkyl sulfates which are always formed when olefins are treated with sulfuric acid, and which tend to break up (even in storage at atmospheric temperatures) into complex alcohols and sulfuric acid. This freeing of sulfuric acid from its esters is no doubt often responsible for a large portion of the acidity which develops in all lubricating oils on standing, and particularly in service. And it is these decomposed and easily carbonized and corrosive bodies, among others, that would have to stand scrutiny when we decide whether or not the impurities left over from the acid treatment are deleterious, and how they would affect the oil in actual service.

Approaching this question from the angle of oxidization, we must bear in mind the powerful catalytic action exerted by the presence of so-called asphaltic bodies, in encouraging the oxidation of lubricating oils when subjected to moderately high temperatures in the presence of air, thus forming additional gummy, resinous, naphtha-insoluble bodies (as brought out so forcibly by the extensive researches of Mr. Waters of the Bureau of Standards). The close kinship between these asphaltic bodies and the colloidal bituminous bodies of the oil-soluble type derived from neutralized sludges that are discussed in this paper, as well as between the conditions of the oxidation tests conducted by Mr. Waters and those prevailing in the chassis of an automobile, is quite apparent. It seems clear, therefore, that when a substantial amount of such bodies exists in an oil, as will be revealed in the Conradson test, it may be expected that such an oil will oxidize and gum up readily in service.

From this discussion it would seem plausible that the elimination of all ingredients in mineral lubricating oils which tend to form any kind of emulsified layer, would at the same time tend to cut down the possibility of either cracking or oxidization in the oil in service.

It would no doubt be too radical a demand at this time to require that all oils be acid-treated with such nicety and precision (or that a less perfect treatment be supplemented by such thorough filtering or alcohol purification) that the finished oil will show absolutely perfect demulsibility under the Conradson test, without any trace of emulsified layer; but at least it seems pertinent to suggest the advisability of specifying that where an oil does yield an emulsified layer under that test, it shall be merely of a light, foamy character and not dense and homogeneous.

This phase of the Conradson demulsibility test well merits further study, and while many other demulsibility tests have since been proposed, each of which has many points in its favor, none of the latter seem well adapted for the observation and study of the impurities thrown down by the steaming, as the Conradson method undoubtedly is; and whichever method is finally adopted for the determination of the speed of demulsibility proper, it is hoped the Conradson test will continue serving the chemist, as the criterion of cleanness and purity in oil.

The Examination of Low-Temperature Coal Tars—II[1]

By Jerome J. Morgan and Roland P. Soule

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In a previous instalment of this paper the examination of phenols from low-temperature coal tar has been treated, and a procedure given for separating the hydrocarbons into a portion containing paraffins and naphthenes and another portion containing unsaturated and aromatic compounds. The method for estimating the proportions of constituents in the first portion has been discussed. The present section deals with the separation of aromatic and unsaturated compounds from a mixture. The method finally adopted, after studying various unsuccessful methods of determining each in the presence of the other, as well as the actions of aluminium chloride, sulfuric acid, and mercuric acetate, was extraction by liquid sulfur dioxide, which, when carefully controlled, yielded a fairly pure fraction of unsaturated hydrocarbons on account of the absence of the more than traces of aromatics in the low-temperature tars.

The specific methods for determining unsaturated compounds in the presence of aromatics may be divided into two classes:

I—Methods indicating relative saturation, by determination of:

  (1) Maumene number
  (2) Bromine number
  (3) Iodine number

II—Methods depending on the actual removal of unsaturated hydrocarbons by:

  (1) Aluminium or zinc chloride
  (2) Sulfuric acid of various concentrations
  (3) Mercuric acetate

None of these methods was considered satisfactory as giving accurate data on the percentages of unsaturated hydrocarbons in the mixture in question, but sufficient interest attaches to the investigations to warrant their review here.

Methods Indicating Relative Unsaturation

These methods were investigated with a view to finding a measure of efficiency of separation, since the reduction of 1 per cent potassium permanganate solution proved too delicate to indicate the reduction of unsaturation in the successive steps. The Maumene number, a measure of the temperature rise of a mixture of the oil in question with concentrated sulfuric acid, although thoroughly investigated for light hydrocarbons,[2] was found unreliable, especially for highly unsaturated oils, and was unsuited to modification. A similar investigation has been made[2] of a representative bromine-absorption method,[3] but this was unsatisfactory on account of substitution[4] as well as addition reactions. For this reason the use of the bromine number, even when compensated for substitution reactions, is less desirable than the iodine number.

Iodine Number—A Hanus iodine solution was prepared and used according to standard procedure in the determination of the iodine numbers of low-temperature hydrocarbons after various treatments. The erratic and nonconcordant results obtained prompted an investigation of this method, with the purpose of so standardizing the conditions that consistent data could be secured. The principal factors of consequence were found to be: (1) the ratio of bromine to iodine in the Hanus solution, (2) the weight of sample used, and (3) the time of reaction.

The effect of a change of the bromine-iodine ratio under similar experimental conditions upon a hydrocarbon sample obtained in the course of treatment of Fraction 237°–287° C. was studied. The iodine number was 80 when the Hanus solution contained very nearly the prescribed atomic proportions of bromine and iodine. This value was increased to 124 by adding more bromine to the solution, and decreased to 73 by adding more iodine. The changes made in the ratio were somewhat greater than would be encountered in ordinary practice, but serve to emphasize the necessity of bringing a Hanus solution to exactly the same strength and proportions if strictly concordant results are to be expected. Moreover, even a slight increase of bromine over iodine accentuates the dependence of the iodine number upon the weight of sample.

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[1] Presented before the Section of Gas and Fuel Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. Part I appeared in the June issue of This Journal.

[2] Dean and Hill, *Bur. Mines, Tech. Paper* **181** (1917).

[3] McIlhiney, *J. Am. Chem. Soc.*, **21** (1899), 1084.

[4] Fischer and Gluud, *Ges. Abhandl. Kenntnis Kohle*, **2** (1917), 315, experienced difficulties from substitution reactions in the use of the bromine number as a test of the degree of refining of low-temperature benzines.

An increase in the weight of the sample taken, or a decrease in the excess of the reagent used, was found to lower the iodine number greatly. Consistent results could not be secured, moreover, even when the recommended excess of 60 per cent of the reagent was greatly exceeded. Table I summarizes a typical experiment made with a Hanus solution containing slightly more iodine than bromine, and used with a minimum excess of 80 per cent. The oil employed was a sample of Fraction 173°–237° C. of a low-temperature tar, from which a portion of the unsaturated compounds had been removed. The decrease in the iodine number with slight increases in the weight of the sample is very marked and uniform.

TABLE I—VARIATION OF IODINE NUMBER WITH WEIGHT OF SAMPLE

Weight Sample G.	Iodine Number
0.1090	56.3
0.1331	52.2
0.1515	49.8
0.2000	44.9

TABLE II—VARIATION OF IODINE NUMBER WITH BOILING POINT OF SAMPLE

Fraction B. p. ° C.	Depression per Mg.
20 to 173	0.02
173 to 237	0.11
237 to 281	0.18
281 to 315	0.26
315 to 326	0.30

Table II shows that this functional variation of the iodine number with the weight of the sample depends upon the boiling point, or molecular weight, of the oil examined, and is greatest in the highest boiling fractions. This set of figures was obtained with a Hanus solution containing a marked excess of iodine over bromine, and represented conditions of minimum fluctuation. Each unit depression of the iodine number per millogram increase in the weight of sample taken for analysis holds only in the neighborhood of 100-mg. samples, since the relationship is not quite linear. Each value tabulated is the mean of at least six pairs of determinations of the iodine numbers of the respective fractions in various stages of the removal of the unsaturated hydrocarbons. It is evident that the iodine numbers of the first fractions are practically independent of the weight of the sample, while that of the highest fraction decreases by nearly one unit for each increase of 3 mg. over the 100-mg. sample.

The iodine numbers become larger when added time is allowed for reaction. Thus, a sample of treated oil from Fraction 237°–281° C. increased from 80 to 93 in an additional 30-min. digestion. This factor is readily controlled, of course, but serves to emphasize the empirical nature of the determination.

A consideration of these data leads to the following conclusions:

(1) The iodine numbers determined in the hydrocarbons of low-temperature tar are all lower than the theoretical value, the difference being least in the first fraction and greatest in the fraction of highest boiling point.

(2) They approach the theoretical values more closely as smaller samples are taken for analysis, as larger excesses of the reagent are employed, as longer time is allowed for digestion, and as larger proportions of bromine to iodine are employed.

(3) When the ratio of bromine to iodine exceeds the atomic proportions, however, substitution reactions cause a large and fictitious increase in the iodine numbers.[5]

Since the completion of these experiments a thorough study has been reported[6] of the determination of the iodine numbers of cracked gasolines, and of the olefins, diolefins, and other compounds which they are likely to contain. The maximum values obtained with the Hanus solution as ordinarily prepared were stated to give the true unsaturation of olefins. In this case, the effect of variations in the weight of the sample was the reverse of that reported for the low-temperature tar hydrocarbons—i. e., greatest for compounds of lowest molecular weight. This was explained by the fact that for a given weight of olefin the same quantity of reagent furnishes a greater excess for a substance of high than for one of low molecular weight. Unsaturated hydrocarbons such as occur in low-temperature coal tars contain several double bonds, however, and, like the diolefins, behave quite differently from the olefins.

All iodine numbers reported in the following experiments were obtained with a Hanus iodine solution containing an excess of iodine over bromine. This solution was always used in 80 per cent excess with a 30-min. period of digestion. Determinations were made in duplicate, with one sample slightly heavier and the other slightly lighter than 100 mg. The reported value was found by interpolation for 100 mg. While such results have small theoretical significance, they are strictly comparable one with another, and permit a quantitative study of the progress of the removal of the unsaturated hydrocarbons.

REMOVAL OF UNSATURATED HYDROCARBONS

ALUMINIUM AND ZINC CHLORIDES—The functions of anhydrous aluminium chloride as an agent in the removal of unsaturated compounds[7] from hydrocarbon mixtures lie in its ability (1) to form addition compounds with them, and (2) to polymerize them to a tar. Zinc chloride has the same effect. Thus, if the mixture is agitated with the reagent and then redistilled, the distillate is found to contain a smaller proportion of unsaturated compounds. This procedure has been employed in the treatment of the benzine from low-temperature tars[4] with the production of products stable to light and air, although the distillate had a higher density than the original mixture and still contained unsaturated compounds. An added objection is the possibility of interaction between the aluminium chloride and any higher aromatic hydrocarbons which may be present.[8] This process, therefore, has more to commend it as a method of refining than of analyzing low-temperature hydrocarbons.

SULFURIC ACID—The use of sulfuric acid has been the almost universal method of removing and estimating unsaturated hydrocarbons either in the presence or absence of aromatics. The conditions have varied widely—concentrations from 80 per cent to oleum, proportions from 5 to 200 per cent by volume, and temperatures from 0° C. to the boiling point of the oil have been employed. It was known to the advocates of this procedure that strong agitation with 200 per cent by volume of 95 per cent sulfuric acid as a method[9] of estimating unsaturation results in the partial sulfonation of any aromatics, such as xylene, which may be present. Nevertheless, its application has not been confined to oils of negligible aromatic content. Equal volumes of 95 per cent acid have been employed[10] to remove olefin preliminary to the estimation of aromatic hydrocarbons, and twice this ratio in the determination of unsaturated compounds in shale oils[11] in which aromatic hydrocarbons also occur. Moreover, the solution of the polymerized unsaturated hydrocarbons in the neutral residue, and in some cases the presence of acid-soluble bases, have also been neglected.

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[5] Johansen, THIS JOURNAL, **14** (1922), 288, reports substitution reactions in petroleum products with the standard Hanus solution.

[6] Faragher, Cruse, and Garner, THIS JOURNAL, **13** (1921), 1044.

[7] Heusler, *Z. angew. Chem.*, **9** (1896), 288, 318; Henderson and Gangloff, *J. Am. Chem. Soc.*, **38** (1916), 1382; Gangloff and Henderson, *Ibid.*, **39** (1917), 1420.

[8] Moore and Egloff, *Met. Chem. Eng.*, **17** (1917), 61, 128.

[9] Dean and Hill, *loc. cit.*, developed a Babcock bottle procedure modified from the suggestion of Egloff and Twomey, *Met. Chem. Eng.*, **14** (1916), 247.

It is only fair to state, however, that in general these investigators have not been blind to the errors inherent in their procedures. Experience has shown that there is no concentration of acid capable of removing the olefins, except very approximately, without at the same time attacking the aromatics, or even the naphthene and paraffin hydrocarbons. There seems no escape from the conclusion[12] that there is at present no method for the quantitative determination of unsaturated hydrocarbons. In the absence of a more specific reagent, however, recourse has been taken to concentrated sulfuric acid as a means of securing results that are at least of comparative value.

Several experiments with sulfuric acid under various conditions were made with the hydrocarbon mixtures from a low-temperature tar. Since most of the data reported in the literature deal exclusively with the olefins, it seemed advisable to subject the cyclic unsaturated compounds of low-temperature tars to further study. The results served chiefly to emphasize again the shortcomings of the sulfuric acid method.

Experiments on the sulfonation of commercial xylene with an excess of acid (two to three volumes) proved that sulfonation takes place slowly but continuously in the cold with all concentrations of acid above 80 per cent. A sample of xylene was reduced to one-third of its original volume after 5 hrs. agitation with an equal volume of 95 per cent sulfuric acid. The sulfonation was only 0.45 per cent, however, when acid of the same strength was used with ten volumes of the oil. These blank runs must be borne in mind in considering the following results.

The lower fractions of the low-temperature tar hydrocarbons proved more amenable to acid treatment than the higher fractions, and were studied more extensively. Fraction 173°–237° C. was subjected successively to five treatments at room temperature with 80 per cent, six with 82 per cent, three with 85 per cent, and two with 90 per cent sulfuric acid, in proportions ranging from 25 to 50 per cent of the oil, and over periods of agitation varying between 20 min. and 20 hrs. The iodine number was reduced rapidly in the first treatments, but with decreasing decrements in the last ones. Unsaturated hydrocarbons survived this treatment in considerable quantity. The relative effectiveness of the various steps in this procedure may be summarized as follows: 14 hrs. agitation with an equal volume of 80 per cent acid reduced the iodine number from 84.7 to 58.1; a similar second treatment from 58.1 to 50.6; and finally, after three more treatments with equal volumes of 85 per cent acid, the iodine number became 20.6. On the other hand, 14 hrs. agitation of the same sample with an equal volume of 95 per cent acid reduced the iodine number from 84.7 to 9.3, but the conditions permitted sulfonation.

Experiments in which the oil was refluxed at its boiling point with 80 per cent sulfuric acid in varying proportions[13] were only slightly more successful. An equal volume of acid reduced the iodine number from 84.7 to 33.0, while a volume twice that of the oil resulted in a number of 27.5. This procedure, moreover, gave rise to the formation of a large quantity of pulverulent coke in the flask, and the quantitative separation and purification of the residual oil involved considerable experimental difficulty.

The remaining experiments dealt chiefly with the effect of small quantities of acid of relatively high concentration. Using 90 per cent acid in proportions of 5 to 25 per cent by volume of the oil, it was found possible to reduce the iodine number of a sample of Fraction 20°–237° C. from 84.7 to 26.8 in eight successive treatments. Ninety-five per cent acid was then substituted for the purpose of increasing the experimental accuracy by a reduction in the number of treatments. It was employed in each case in the proportion of about 10 to 15 per cent by weight of the oil, and thus approximated conditions in the commercial refining of petroleum[14] and of light coal-tar distillates.[15] Agitations were performed at room temperature, and from 20 to 30 min. were allowed for each treatment, experiments having demonstrated that little gain was secured by longer shaking. The results of these treatments are recorded in Table III:

TABLE III TREATMENT OF LOW TEMPERATURE TAR HYDROCARBONS WITH 95 PER CENT SULFURIC ACID

	20°–173° C.		173°–237° C.		237°–281° C.		281°–315° C.		315°–326° C.	
No.	Wt. G	I No.	Wt. G	I No.	Wt. G	I No.	Wt. G.	I No.	Wt. G.	I No.
0	50.0	116.0	50.0	95.5	50.0	85.3	50.0	80.1	50.0	79.6
1	45.6	95.7	47.2	90.6	45.6	72.4	45.2	74.4	44.7	76.2
2	43.4	79.7	43.8	69.7	43.9	62.1	42.9	65.6	42.0	70.6
3	42.1	66.9	41.9	51.6	42.8	54.1	41.5	60.0	40.4	69.2
4	40.8	59.2	40.4	41.8	41.6	47.7	40.3	58.4	38.4	68.8
5	39.7	50.8			40.3	46.4	39.3	54.1	37.1	68.7
6	39.1	46.4	....	....	....	....	....	....	....	....
7	38.7	43.9								
8	37.6	40.0								
9	37.1	39.0	....	....	....	....	....	....	....	....

A 50-g. sample of each fraction was agitated with 10 to 15 per cent by weight of 95 per cent sulfuric acid for 20 to 30 min., and the layers allowed to separate in a 50-cc. buret. The quantity of residual oils was determined by direct weighing of the buret and its contents. A very small sample was removed in each case, and washed with alkali for the iodine number determination. Correction for this sampling has been made in the recorded data. Each fraction was treated in duplicate for the entire series of agitations, and the closely concordant results obtained demonstrated the reliability of the methods employed, both in the weighings and in the iodine number determinations.

These results are given in Fig. 1, in which the iodine numbers have been plotted against the percentages of decrease in weight. The iodine numbers have also been plotted against the average boiling points of the respective fractions.

The curves showing the variation of the iodine numbers with the percentage decrease in weight of each fraction are instructive. The upper ranges of these curves should be convex in the opposite direction, if it may be presumed that the more active compounds, which have the lowest molecular weights and the highest iodine numbers, are the first to be acted upon. That the reverse situation is true may be explained readily on the basis of polymerization,[12] which tends to lower the iodine numbers without a corresponding reduction in the weight of the residual oils.

Confirmatory evidence supporting this conclusion was noted during the experiments. Thus, the curve could be made much steeper if the residual oil was not separated immediately from the acid after treatment, but was allowed to stand in contact with it for several days. Moreover, much tar was formed in the early treatments of each fraction. Since olefins do not polymerize to tars, this has been cited[12] as a characteristic of diolefins. It may be pointed out in this connection that the cyclic unsaturated compounds of low-temperature tars are reported[16] to contain from two double bonds in the lowest to five in the highest boiling fractions. Finally, polymerization was also evident from the increase in density of the residual oils in the lower fractions, since the removal of unsaturated compounds alone should not lower the density. This increase in density was less marked in the higher fractions and disappeared in Fraction 281°–315° C. because of the insolubility of the tarry polymers. The highest boiling fraction showed a slight decrease in density.

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[10] Rittman, Twomey, and Egloff, *Met. Chem. Eng.*, **13** (1915), 682; Moore and Egloff, *Ibid.*, **17** (1917), 297.

[11] Botkin, *Ibid.*, **24** (1921), 876; Franks, *Ibid.*, **25** (1921), 731.

[12] Brooks and Humphrey, *J. Am. Chem. Soc.*, **40** (1918), 822.

[13] Hackford, discussion of paper by Thole, *J. Soc. Chem. Ind.*, **38** (1919), 42.

[14] Bacon and Hamor, "The American Petroleum Industry," **2** (1916), 460.

[15] Dodge, Allen Rogers' "Manual of Industrial Chemistry," **1920**, p. 563.

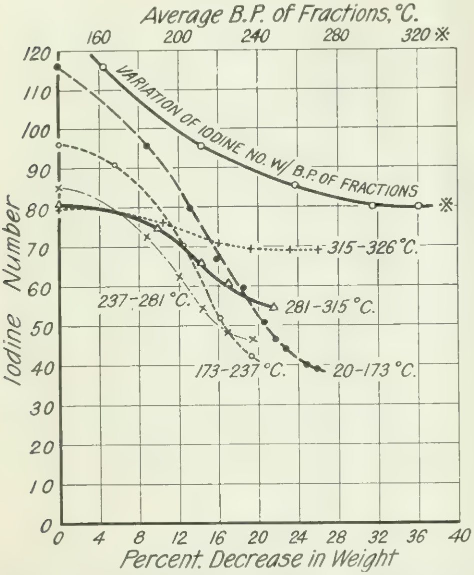

Fig. 1—Relation between Loss of Weight and Iodine Number of Low-Temperature Tar Hydrocarbons when Treated with 95 Per cent Sulfuric Acid

These facts lead to a consideration of the lower sections of the curves of Fig. 1. All show a well-defined point of inflection, beyond which the predominating effect is not polymerization, but a reaction involving the elimination of a portion of the saturated components. In Fraction 315°–326° C. this effect balances the removal of the unsaturated compounds to such an extent that the iodine number remains almost unchanged after the first two treatments. It thus becomes apparent that the use of 95 per cent sulfuric acid under these conditions is ineffective in the complete removal of unsaturated compounds, and that in the higher fractions the saturated hydrocarbons also are attacked.

Mercuric Acetate—Digestion with mercuric acetate has been advocated[17] as a volumetric method for the quantitative estimation of olefins in petroleum oils. It is stated that if this salt is refluxed for 8 hrs. in dilute alcohol solution with the oil, it will combine with some of the unsaturated hydrocarbons and oxidize the others. The saturated residual oils may then be distilled off with steam, and the addition compound remaining decomposed with concentrated mineral acid to regenerate the olefins.

The application of this procedure to low-temperature tar hydrocarbons has not been attended with any marked success. The higher fractions in particular proved relatively inert toward this reagent, and only slight reductions in the iodine number were obtained. Moreover, the "apparatus constant," or loss sustained in a blank test with a saturated sample, was a large and uncertain factor in these oils of high boiling point. Thus, less than 50 per cent of the volume of sample of Fraction 281°–315° C. could be steam-distilled from the digestion flask in 5 hrs., and the problem of condensing involved further error. The attempt to substitute extraction for steam distillation was unsuccessful.

The low-boiling fractions proved to be the best adapted to treatment with mercuric acetate. While no more than a single treatment with mercuric acetate has been specified[17] for this method, multiple digestions were found necessary to make any considerable progress. Two successive treatments of Fraction 173°–237° C. reduced the iodine number from 84.7 to 54.8 to 41.3. Four successive treatments reduced the iodine number of Fraction 20°–173° C. from 116.0 to 16.6. The results of this series of runs are plotted in Fig. 2, together with the curve representing the sulfuric acid treatment of the same fraction (Fig. 1).

These digestions were made with oil and mercuric acetate in the ratio of about 1:2 by weight. The salt was dissolved in a large excess of water containing 10 per cent of alcohol. Each sample was refluxed about 10 hrs. and then steam-distilled in the usual manner. The curve indicates a minimum amount of polymerization. This is confirmed by the fact that the density was reduced from 0.814 to 0.806 in the four treatments. It is apparent that an extension of the curve can be made to intersect the horizontal axis at a point corre-

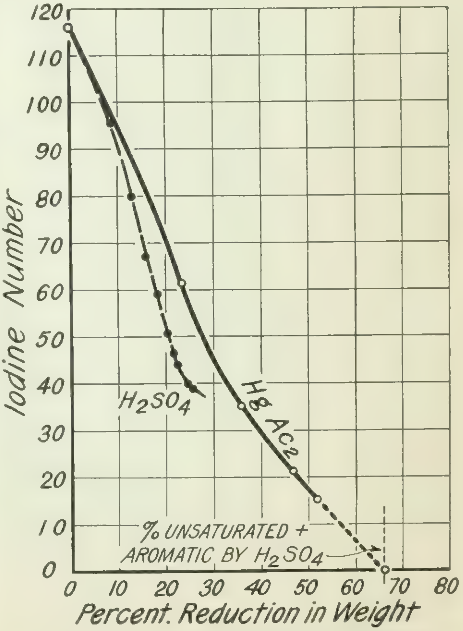

Fig. 2—Relation between Loss of Weight and Iodine Number of Low-Temperature Tar Hydrocarbons, Fraction 20°–173° C., when Treated Successively with Mercuric Acetate or with 95 Per cent Sulfuric Acid

sponding with the percentage of unsaturated plus aromatic hydrocarbons (determined by 98 per cent sulfuric acid) in the neutral oils of this fraction. Since blank runs show the mercuric acetate to be without effect on aromatics such as xylene under the conditions of the experiment, this extrapolation may be taken as confirmatory evidence of the great preponderance of unsaturated over aromatic hydrocarbons in the low-boiling fractions of low-temperature tars.

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[16] Pictet, *Ann. chim.*, [9] **10** (1918), 249.

[17] Tausz, Inaugural Dissertation, Karlsruhe, **1911**; *Chem. Ztg.*, **42**, (1918), 349; *Petroleum*, **13** (1918), 649; Tausz and Wolf, *Z. angew. Chem.*, **321** (1919), 317.

Two observations cast some doubt on the exactness of the mercuric acetate method. In the first place, slight polymerization is indicated by the shape of the upper half of the curve and by the fact that the decrease in density is less than would be expected from so great a reduction in the iodine number. Furthermore, the mercuric acetate seems to remove from the oil small amounts of saturated components. This is indicated by low iodine numbers of the "unsaturated" hydrocarbons recovered by acidifying the residual addition compound and steam-distilling. These two factors are opposite in effect, the first tending to shift the curve slightly to the left and the second to the right, and apparently they almost balance each other.

Recovery of Unsaturated Hydrocarbons of Low-Temperature Tar

A convenient method for recovering the unsaturated (and aromatic) hydrocarbons comparatively free from naphthenes and paraffins is extraction with liquid sulfur dioxide. It has been pointed out above that the hydrocarbon Fraction 20°–173° C. of a low-temperature tar proved miscible with this solvent in all proportions at −35° C., but further investigation reveals the fact that the separations accomplished are more specific in mixtures of higher average molecular weight. Nevertheless, some doubt must be cast on the purity of the hydrocarbons thus extracted from a sample of the entire series of compounds in a low-temperature tar, in view of the variation in the effect of the solvent throughout the wide range of compounds involved. In particular, it is to be expected that the lower fractions will be found admixed with a portion of naphthene and paraffin hydrocarbons. In most low-temperature tars the proportion of aromatics is so small that the sulfur dioxide extract is composed almost entirely of the cyclic unsaturated hydrocarbons. These compounds may be further investigated, as indicated in an earlier paper.[18]

A study of the various designs of apparatus and methods of procedure[19] in the use of liquid sulfur dioxide points to the scheme devised by Bowrey[20] as the most effective and convenient. This method does away with freezing mixtures and accomplishes effective cooling and agitation simultaneously by boiling the mixture of oil and solvent in a vacuum bottle under greatly reduced pressure. Temperatures of −35° C. are readily obtained. After the layers have separated, the reaction mixture is siphoned into a separatory funnel connected with a water vacuum pump, and the sulfur dioxide allowed to evaporate off slowly. Working with a mixture of all the fractions of a low-temperature tar distillate, a good separation of layers was accomplished by this siphoning process alone. The top layer, consisting principally of a mixture of naphthenes and paraffins, proved too viscous at −35° C. to pass through the small-bore siphon tube, and remained behind in the vacuum bottle.

After studying the effectiveness of various separations made with oil and solvent in different proportions, a ratio of three parts by volume of the hydrocarbons to five parts of the sulfur dioxide was found most practicable. It has been pointed out[21] that naphthenes of low molecular weight are increasingly soluble in excesses of liquid sulfur dioxide, but this solubility was not evident in the mixture examined. The density of the extract continued to increase with greater excesses of solvent, and a practical limit to the most effective ratio of solvent to oil was reached only because the elimination from the extract of a large excess of sulfur dioxide involved considerable loss by evaporation of the more volatile hydrocarbons.

[18] Morgan and Soule, *Chem. Met. Eng.*, **26** (1922), 980.

[19] See Footnotes 28 and 29 in Part I.

[20] Bowrey, *J. Inst. Petroleum Tech.*, **3** (1917), 287; *Chem. Trade J.*, **60** (1917), 426.

[21] Moore, Morrell, and Egloff, *Met. Chem. Eng.*, **18** (1918), 396.

The Methoxyl in Wood Charcoal[1]

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In a former article[2] it was concluded that wood charcoal contains a small proportion of methoxyl groups which respond to the Zeisel method of analysis, and probably a much larger proportion which form methane when the charcoal is heated from 450° to 900° C. It was also determined that about one-third of the methoxyl groups in the original wood were left in the charcoal after the ordinary destructive distillation process was finished. This note is a report of attempts to recover this methoxyl in the form of methanol instead of methane.

Following the line of attack used in previous work on increasing yields of methanol from wood,[3] various chemicals were added to the charcoal and the mixture was distilled at high temperatures (maximum about 850° C.). Since the amount of liquid products obtained from charcoal in this manner is very small and the amount of gas very large, it is necessary to scrub the gas in large quantities of water in order to recover so volatile a product as methanol. In blank distillations without the addition of any chemical about 0.3 per cent of methanol on the weight of the charcoal used was recovered, less than one-third of this coming off below 730° C. This is the first time that methanol has been reported as a product of the distillation of charcoal at temperatures above those used in the normal wood distillation process.

Sodium carbonate, lime, phosphoric acid, calcium carbonate, sodium sulfate, magnesium carbonate, and potassium permanganate were used for treating the charcoal in attempts to increase this yield of methanol. Only in the case of lime and of calcium carbonate was there any increase in the amount of methanol and this increase was only slight, the total methanol yield being only 0.5 per cent. Charcoal was also distilled in slow currents of carbon dioxide, air, steam, and various mixtures of these, but only in the carbon dioxide was any appreciable increase in yield obtained. When the charcoal was heated in a slow current of carbon dioxide the yield of methanol was 0.5 per cent.

The increase in yields obtained was so small and the apparent chances for further increases so poor that the work was discontinued at this stage.

[1] Presented before the Division of Cellulose Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Hawley and Aiyar, This Journal, **14** (1922), 1055.

[3] Hawley, *Ibid.*, **14**, (1922), 43.

The Removal of Small Amounts of Carbon Monoxide from Gases by Passage through Heated Granular Soda Lime[1,2]

By Robert E. Wilson, C. A. Hasslacher, and E. Masterson[3]

Massachusetts Institute of Technology, Cambridge, Mass.

The problem of the complete removal of carbon monoxide from gas streams is of importance in a number of industrial applications, particularly in the purification of hydrogen and nitrogen for the synthesis of ammonia. Several references and patents have mentioned the use of soda lime at high temperatures for this purpose, but practically no quantitative data are offered with regard to the removal of small amounts, or the effect of the composition of the soda lime.

This paper describes a series of experiments on gas containing 2 per cent carbon monoxide in nitrogen, at temperatures varying from 250° to 550° C., and using soda limes of varying composition. The results show that soda limes with high caustic soda contents are better than those with low, or than lime alone. The former give substantially complete removal of carbon monoxide at around 400° C. Small amounts of moisture are helpful in increasing the efficiency, but do not appear to be essential. Experiments in the presence of hydrogen are inconclusive because the hydrogen used reacted slightly with the iodine pentoxide used to determine carbon monoxide.

The fundamental reaction for the removal of carbon monoxide at the higher temperatures is apparently:

$$CO + 2NaOH = Na_2CO_3 + H_2$$

THE removal of small amounts of carbon monoxide from gas streams is of importance in a number of industrial applications. A frequent cause necessitating its complete removal is its pronounced tendency to poison the catalyst in various catalytic reactions.

Probably the largest scale application in which this problem is important is in the nitrogen fixation industry. The hydrogen for making synthetic ammonia is generally produced from water gas, the carbon monoxide being removed either by catalyzing its decomposition into carbon dioxide and carbon at elevated temperatures, or, more frequently, by oxidizing it with steam in the presence of a catalyst such as ferric oxide at temperatures between 400° and 600° C.[4] Neither of these processes is capable of the complete removal of the carbon monoxide, and a number of other methods have therefore been developed for taking care of the last 2 or 3 per cent. Ammoniacal solutions of cuprous formate or cuprous carbonate have been used on a large scale,[4] but the cost of the solutions is high and it is difficult to secure complete removal. Differential oxidation processes have also been tried with some success, although these reactions are very difficult to control on a large scale if more than a trace of carbon monoxide is present.

Attempts have also been made to make use of the reaction

$$CO + NaOH = HCOONa$$

which has been successfully utilized for the production of sodium formate. While this reaction proceeds fairly rapidly at temperatures around 250° C. and pressures in the neighborhood of 50 atmospheres for gases rich in carbon monoxide, it is not adapted to the complete removal of small amounts. Furthermore, the handling of hot caustic solutions in such a way as to bring them into effective contact with gas under high pressure is a very difficult proposition from a mechanical standpoint, and as yet has not been worked out in a satisfactory manner.[4]

There are several references in the literature to the use of granular soda lime for carrying out a similar reaction. Thus, as far back as 1877, Merz and Tibirica[5] were able to form some calcium and some sodium formate by passing high concentrations of carbon monoxide over soda lime, but they were not primarily interested in the completeness of its removal. Two later papers[6] presented the results of a more detailed study which indicated that the presence of moisture was necessary to give a satisfactory rate of absorption, and that a soda lime containing 50 per cent sodium hydroxide gave very rapid absorption, with the production of formate, at a temperature at 220° to 230° C. At higher temperatures the absorption was even more rapid, but resulted in the production of equivalent amounts of hydrogen and carbonate. Apparently, the reaction may proceed in steps

$$NaOH + CO = HCOONa \qquad (1)$$

$$2HCOONa = Na_2CO_3 + CO + H_3$$

with the readsorption of the carbon monoxide by the first reaction, but at any rate the net effect is

$$2NaOH + CO = Na_2CO_3 + H_2 \qquad (2)$$

which is obviously closely related to the reaction mentioned previously for the removal of carbon monoxide:

$$H_2O + CO = CO_2 + H_2 \qquad (3)$$

except that the equilibrium is displaced to the right by the absorption of the carbon dioxide by soda lime.

Based on this reaction, a British patent[7] was granted in 1889 for rendering water gas nonpoisonous by passing it through a layer of soda lime several feet thick at a "good red heat."

In 1912, a German patent[8] was issued for a process of removing carbon monoxide and dioxide from water gas by passing over lime or soda lime heated to a temperature somewhat below a red heat. A similar patent[9] was issued during the same year to other parties. None of the patents gives any significant quantitative data, however.

An obscure reference by Engels[10] gives the best discussion of the fundamentals of the reaction between carbon monoxide and calcium hydroxide alone at the higher temperatures. He recommends a temperature around 500° C., with just enough steam to prevent dehydration of the calcium hydroxide. He finds that the rate of reaction is markedly catalyzed by "iron" (ferric hydroxide?) due to its previously mentioned catalytic effect on Reaction 3.

In spite of these interesting statements, and the obvious advantages of using a hard, granular absorbent such as soda

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Published as Contribution No. 65 from the Research Laboratory of Applied Chemistry, M. I. T.

[3] Most of the work described in this paper was carried out by the two junior authors as part of their theses for the degree of Bachelor of Science from M. I. T.

[4] This Journal, **12** (1920), 851.

[5] *Ber.*, **10** (1877), 2117.

[6] Merz and Tibirica, *Ber.*, **13** (1880), 23; Merz and Weith, *Ibid.*, **13** (1880), 718.

[7] Brit. Patent 10,164.

[8] D. R. P. 248,290, to the "Société Général des Nitrures" in Paris.

[9] Brit. Patent 13,049 (1912), to the "Chemische Fabrik Griesham-Electron."

[10] *C. A.*, **14** (1920), 599.

lime, rather than loose, hydrated lime or molten caustic, so far as the writers are aware, soda lime has never been utilized commercially for the removal of carbon monoxide, and no quantitative study has been made of its absorption efficiency as a function of its composition and temperature.

Previous investigations in this laboratory[11] on the efficiency of various kinds of soda lime as an absorbent for other gases had shown that its absorption efficiency varied greatly with composition, and that a low caustic soda content (about 4 per cent sodium hydroxide, hereinafter referred to as the "low alkali" soda lime) and a fairly high moisture content (12 to 18 per cent, depending on the gas to be absorbed) gave far better efficiency than ordinary, commercial, high-alkali soda limes, and had the additional advantage of not deliquescing in moist atmospheres.

It was therefore decided to undertake a quantitative investigation of the absorption of carbon monoxide by soda lime, studying particularly the effect of temperature, moisture content, and alkali content of the soda lime on its efficiency in removing small amounts of carbon monoxide from gas streams. The treatment of more concentrated mixtures, such as water gas, was considered to be of less practical interest, because the chemical cost would be high compared to other methods mentioned above by which the bulk of the carbon monoxide may be converted to carbon dioxide.

APPARATUS AND PROCEDURE

It appeared from the literature as summarized above, that soda lime at temperatures in the neighborhood of 230° C. would have promising possibilities, in that it should not only absorb the carbon monoxide, but give formates as a valuable by-product. The first experiments, therefore, were carried out at temperatures obtainable in an oil bath.

The apparatus consisted essentially in a gas holder containing 98 per cent nitrogen and 2 per cent carbon monoxide (the latter made by the action of sulfuric acid on sodium formate) which fed through a train comprising:

(*a*) A carefully calibrated flowmeter with inclined manometer arms.

(*b*) A wash bottle containing alkaline pyrogallol to remove any trace of oxygen (and incidentally any carbon dioxide).

(*c*) A humidifier, consisting of two gas wash bottles containing water, and immersed in an electrically heated bath whose temperature was controlled so as to give any desired moisture content (0[12] to 40 per cent by volume) to the gas passing through, the exit tube being heated to prevent any condensation.

(*d*) A Pyrex preheating coil immersed in another electrically heated and stirred oil bath (later a lead bath).

(*e*) A long armed U-tube of Pyrex glass containing a 13-cm. layer of soda lime and immersed in the same bath as (*d*).

(*f*) A calcium chloride drying train.

(*g*) A connection through which a gas sample could be slowly drawn off into a gas buret.

(*h*) A vacuum regulator (about 6-in. water suction) and thence to the vacuum line.

Thermometers were inserted in the water bottles in the humidifier and one on each side of the U-tube. Thanks to the preheating coil, plus the rather large radiation effects on the thermometers, the recorded temperatures at the entrance and exit of the soda lime were always very nearly the same.

Some preliminary experiments around 200° C. indicated that a velocity of 50 cc. (measured as dry gas at room temperature) per minute gave a readily measurable removal, and this rate was accordingly adopted as standard for all runs, although considerably higher velocities might well have been used at higher temperatures.

An 8-hr. run at this rate indicated no falling off in the efficiency of the soda lime, but as a factor of safety it was always renewed after the gas had been passed through for 2.5 to 3 hrs.

Ten grams of soda lime were used, and gave a depth of about 13 cm. in the tube, which was almost exactly 1 sq. cm. in area. Since the gas was measured dry and at room temperature, the apparent time of contact of gas with soda lime obviously varied considerably with temperature and moisture content, but for the most of the experiments was between 4 and 8 sec.—in other words, it approximated practicable operating conditions for a commercial process.

Most of the runs were made with two commercial soda limes, one containing 4 per cent and one 40 per cent sodium hydroxide. Both samples were screened to 8–14 mesh. The initial water content of the samples was not important as it very quickly reached equilibrium with the air streams. The most extensive tests were made with the low-alkali soda lime, as it was the first one studied and showed a very interesting variation with temperature.

The customary procedure was to bring the humidifier and U-tube to the desired temperature and pass the gas through for about 15 min. before drawing off a sample of the gas for analysis.

The quantitative determination of carbon monoxide was made by passing the sample slowly through a tube of iodine pentoxide at 150° C., sweeping out with nitrogen and absorbing the liberated iodine in 3 per cent potassium iodide, titrating with thiosulfate. The procedure and precautions used were essentially those described in detail by Graham,[13] except that it was found preferable to keep the temperature of the bath at 150° C., thus preventing any condensation of iodine in the exit tubes and speeding up the determination. At the outset of the work an old sample of iodine pentoxide was used, and even using all the known precautions it was impossible to get a satisfactory blank when pure air was sucked through the apparatus. Two fresh samples were later secured, which gave quite satisfactory results provided they were pretreated by passing a current of dry fresh air through them for a period of 20 hrs. at 220° to 230° C.

It was found to be essential that the air used for sweeping out the tube not be taken from the room, where it was contaminated by fumes from the oil bath, nor sucked in through old rubber tubing, as high blanks would result in each case. Nitrogen from a cylinder was used for most of the work. It was also found that small amounts of hydrogen, such as those produced in absorbing the carbon monoxide, did not appreciably affect the results, but attempts to use a gas mixture containing 98 per cent hydrogen gave large and variable blanks, as pointed out later. This might possibly have been overcome by working at somewhat lower temperatures, as recommended by Graham.

Check analyses were made on practically every run, and by comparing the average of these two determinations with the original concentration (1.99 per cent carbon monoxide for most of the runs) the percentage absorption of carbon monoxide could be calculated with accuracy.

EXPERIMENTAL RESULTS WITH LOW-ALKALI SODA LIME

The first series of determinations (by Hasslacher) was made between 180° and 300° C. with one run at 340° C. The two typical curves for 200° and 300° C. are shown in Fig. 1 (dotted lines).

These results indicated that the rate of absorption of such dilute mixtures at temperatures below 250° to 300° C. was so slow as to be of very doubtful commercial value for carbon monoxide removal, although for the production of formate it might be worthy of further consideration. However, the apparent rapid increase in the rate of reaction with temperature in this vicinity indicated the desirability of extending the study to much higher temperatures, for most of which work a lead bath was employed. It was then easily possible to go up to 550° C., which was the safe limit for the Pyrex glass U-tube.

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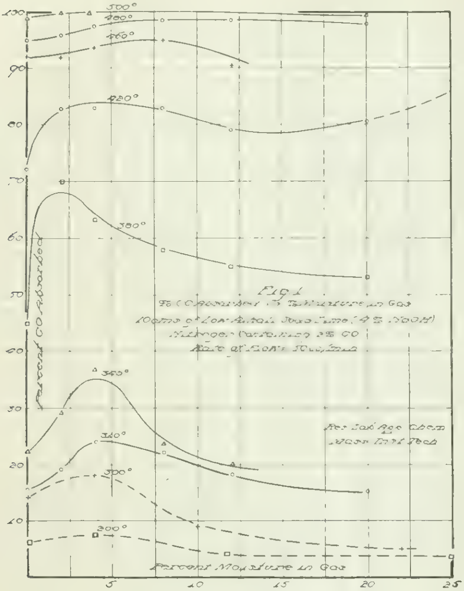
[11] THIS JOURNAL, **12** (1920), 1000.

[12] For the dry air runs the gas by-passed the humidifier through calcium chloride drying train.

[13] *J. Soc. Chem. Ind.*, **38** (1918), 10T.



The second series of results (obtained by Masterson) are shown by the set of full lines on Fig. 1. It will be noted that low temperature results are quite reasonably consistent with those obtained a year earlier with different apparatus and different samples of soda lime, etc. The individual points on the curves were not secured by any regular increase in temperature, but runs at higher temperatures were alternated with runs at lower and intermediate temperatures.

While the shape of the curves varies somewhat from one temperature to another and indicates that there is quite an appreciable experimental error, as might be expected, there can be no real doubt as to the essential conclusions which may be drawn from the work. For example, all the curves in Fig. 1 indicate—contrary to some statements in the literature—that dry gas is absorbed with good efficiency, especially at the higher temperatures, although small amounts of moisture seem to be distinctly helpful in increasing the absorption efficiency, around 4 per cent by volume in the gas apparently being about the optimum for most temperatures. Higher moisture contents appear to injure rather than improve the efficiency.

Fig. 2, based on the same data as Fig. 1, shows the effect of temperature on absorption efficiency for three different moisture contents. It is very interesting to note the sharp rise in efficiency between 320° and 440° C. The fact that formates decompose rapidly around these temperatures to form carbonates may have some bearing on the sharp increase, although the writers obtained no definite evidence of the production of formates as an intermediate step in the reaction. Soda lime used at the higher temperatures showed large amounts of carbonates on removal from the tube.

An experiment was made at a temperature of 420° C. to determine whether or not hydrogen was produced as the result of the absorption of carbon monoxide, and it was found that approximately one equivalent of hydrogen was produced for each equivalent of carbon monoxide absorbed, thus verifying the belief that the fundamental reaction involved was essentially that indicated above (Reaction 2). Tests on the effluent gas at several temperatures showed only a faint trace of carbon dioxide.

Results with Other Absorbents

Experiments were next undertaken on the high-alkali (40 per cent sodium hydroxide) soda lime, and it was at once found that the absorption at intermediate temperatures was much more complete than with the low-alkali soda lime, and that the efficiency of removal did not begin to drop off seriously until about 375° C. The results of these experiments are also shown on Fig. 2.

Runs with straight hydrated lime were attempted, but it was impossible to form it into satisfactory granules or to suck the desired amount of gas through 10 g. of the powdered material. Therefore, 8 to 14-mesh quicklime was used instead, and an attempt made to hydrate it, at least superficially, by passing moist air through for some time at 300° to 400° C.

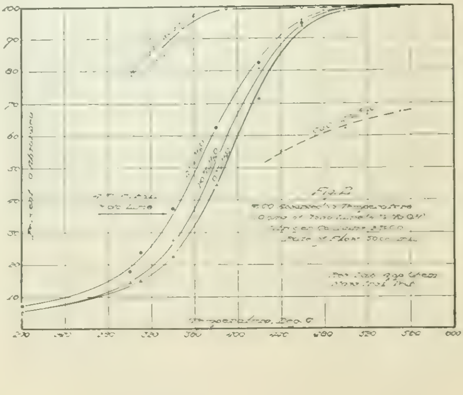
It was found very difficult to obtain check results with this material, but the average of several observations at three different temperatures is shown by the dotted line on Fig. 2. Contrary to the result with soda lime, the efficiency did not remain constant, but dropped off fairly rapidly with time. This may be illustrated by a typical run made at 550° C., using in this case dry gas. Gas samples were taken about every 5 min.

Table I

Run 30, Temperature, 550° C., 0 Per cent Moisture

Sample	Carbon Monoxide Absorbed Per cent
1	88.3
2	81.8
3	84.7
4	75.0
5	63.2
6	63.2
7	56.3
8	55.9
9	55.6
10	54.2

It seems probable that the cause for this rapid drop in efficiency might be the slow dehydration of calcium hydroxide, which has quite an appreciable vapor pressure at this temperature. It is evident that in the presence of dry air the desired reaction cannot take place with calcium oxide, but requires calcium hydroxide. Even with 4 per cent moisture in the gas, however, variable results were obtained, and a similar tendency to drop off in efficiency was observed.



It appears from these results that caustic soda is the active agent in carrying out the desired reaction, but that the caustic soda thus converted to carbonate is slowly regenerated by reacting with the lime. An exactly similar behavior has been observed in the case of soda lime used for absorbing carbon dioxide at ordinary temperatures.

Since hydrogen is a product of the reaction, and the free-energy change at the higher temperatures is probably not great (reversal becomes pronounced at still higher temperatures), it seemed desirable to determine whether or not the presence of large amounts of hydrogen would seriously retard the absorption of the carbon monoxide. A few runs were made with a special hydrogen-carbon monoxide mixture, and the efficiencies obtained at a given temperature appeared to be quite appreciably lower than in the presence of nitrogen, but upon investigating this point further it was found that the hydrogen itself was giving a very large blank with the iodine pentoxide used for the analysis, thus indicating small amounts of carbon monoxide in the effluent gas. This may have been due to the presence of oil vapors in the cylinder hydrogen, or to a reaction of hydrogen itself with iodine pentoxide at this temperature, which is somewhat higher than that recommended by Graham. Unfortunately, time was not available to determine the cause and remedy of the difficulty, but from the size of the blanks with the straight hydrogen the efficiency seems to be nearly, if not quite, as good in the presence as in the absence of hydrogen.

Possible Commercial Applications

In the light of the foregoing experiments it would appear that the reactions under discussion might have definite commercial possibilities for the removal of traces of carbon monoxide from gas streams. It would probably be preferable to use a soda lime of intermediate alkalinity—say 15 per cent sodium hydroxide—in order to secure rapid absorption without undue cost. It would probably be found desirable to work at temperatures of 400° to 450° C. with a time of contact of 2 or 3 sec. This time of contact might have to be increased slightly to remove the very last traces of carbon monoxide, but, on the other hand, it might be reduced by working at somewhat higher temperatures, although too high a temperature (around 700° C.) would undoubtedly give trouble due to the reversing tendency of the reaction in this range.

As noted previously, patents have been taken out for the use of soda lime to remove the bulk, as well as the last traces, of carbon monoxide from water gas, but the chemical cost seems to be too high to make this commercially feasible. It might, however, be practicable to take care of the bulk of the carbon monoxide by either (*a*) passing the gas through a fairly deep bed of high-alkali soda lime at temperatures around 230° C. in order to produce formate as a by-product, or (*b*) removing the bulk of the carbon dioxide with hydrated lime—possibly in the presence of ferric hydroxide as a catalyst—and regenerating the lime by heating somewhat higher and then hydrating.

One difficulty with the latter method would be in handling the powdered lime in such a way as to bring it into effective contact with the gas and avoid trouble from clogging or channeling, but this difficulty would not be insuperable if the process were satisfactory from other standpoints. Since only lime in hydrated form appears to be effective, it would not be possible to use hard granules of quicklime.

On the whole, however, it seems rather improbable that any modification of the soda lime process would be able to replace existing methods of caring for the main bulk of the carbon monoxide in water gas, especially since the oxidation with steam in the presence of ferric hydroxide produces an equivalent of the desired hydrogen for each of carbon monoxide removed.

Hydrogenated Oil for Oil Baths[1]

By G. Ross Robertson

University of California, Southern Branch, Los Angeles, Calif.

"Hard" hydrogenated vegetable oil is a remarkable industrial product which seems to have been overlooked as a laboratory material, probably because it is only an intermediate in the manufacture of shortening, and never reaches the retail trade in a pure state. In this laboratory it has proved to be the oil par excellence for use in oil baths. To anyone who has put up with tarry messes and fire hazards in connection with oil baths in organic laboratories, the properties of this oil should be of interest.

"Hard Sesame Oil"

Opaque white solid, resembling a very brittle laundry soap. Approximately 90 per cent hydrogenated; iodine number about 10. Melts fairly sharply about 60° C. to a clear, mobile oil.

Gives an extremely weak flash in an open pan at a minimum of 320° C.; will not burn unaided by a torch below 350° C., which is approximately the temperature at which it gently boils with decomposition.

Upon resolidification it will not stick to either iron or glass, but cracks and falls apart into brittle fragments.

Slight unpleasant odor, as of unrefined cottonseed oil. Odor is less after repeated heatings.

Cost—in Los Angeles, April, 1923—17.5 cents per pound in small quantities from manufacturer.

This preparation is much superior to vaseline, paraffin, or any other hydrocarbon, is more convenient than untreated vegetable oil, and, of course, much cheaper than fusible metal.

Hard hydrogenated cottonseed oil, more widely obtainable than the sesame product, costs no more and is apparently of about the same value. A local sample, manufactured in Los Angeles, melts at 60° C. and has a flash point of 305° C. The use of this oil has eliminated oil fires in our laboratories, despite the carelessness of elementary students. In commercial practice the hard oil is mixed with cheap liquid or semiliquid fats to make the lower priced shortenings of the type of lard compound.

When vegetable oil is completely hydrogenated, it becomes extremely brittle, and falls into a bulky, semicrystalline powder. Such complete saturation is unnecessary in preparing material for oil bath purposes, and for food is regarded locally as undesirable.

If water is spilled into the melted hydrogenated oil bath, it may easily be removed by cooling the oil, cracking the solid, and exposing to the air. Even if the watery addition has been emulsified, one needs only to crush the material into a coarse, granular mass and expose to dry air.

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[1] Received April 26, 1923.

Saybolt Viscosity Measurements and Their Control[1]

Some Factors Affecting Their Accuracy

By P. E. Klopsteg and W. H. Stannard

Central Scientific Co., Chicago, Ill.

The dependence of viscosity of lubricating oils upon temperatures is too well known to require discussion. The fact that most mineral oils, especially at the lower temperatures of test, have a large temperature coefficient of viscosity, makes precise control of temperature in viscosity tests highly desirable. We may go a step farther and say that accurate measurements cannot be made without such control. The necessity for great constancy of temperature in Saybolt viscosity measurements has been recognized by Committee D-2 of the American Society for Testing Materials, which specifies that "the bath shall be held constant within 0.25° F. (0.14° C.) at such a temperature as will maintain the desired temperature in the standard oil tube," and at another point, "that it is extremely important that the temperature of the oil in the oil bath be maintained constant during the entire time consumed in making the test." In this investigation it was desired to devise means and work out a method which would enable the operator to keep his procedure within the A. S. T. M. specifications.

Proper Circulation in Bath

In working on the problem of constructing a constant temperature bath which should meet the requirements outlined in the synopsis at the beginning of this article, some preliminary experiments confirmed what we had already supposed to be the case—namely, that one of the first essentials for close regulation is proper circulation in the bath. On the basis of the authors' experiments with constant temperature water baths of large dimensions, it was decided that with a propeller of good design, driven at a certain speed, the most thorough mixing and circulating of the bath liquid would be obtained if the bath container were constructed so as to produce "two-dimensional circulation." Accordingly, the container was made narrow, and the corners in the two ends of the bottom of the vessel were rounded. The vessel was made deep enough to accommodate the usual Saybolt oil tube modified by making a higher rim around the top so as to diminish cooling at the surface of the oil sample. The length of the bath was chosen sufficient to accommodate the oil tube near one end and the heating and stirring unit together with the thermoregulator at the other end. Fig. 1 shows the bath in longitudinal section with the direction of circulation of bath liquid indicated.

With this construction, the circulation is approximately the same in any plane parallel to the plane of the figure. The oil is forced over the heating units by the action of the propeller, which thoroughly mixes the warmer with the cooler portions of the oil and rapidly circulates the mixture about the oil tube.[2]

Regulator Used

In the attempt to solve the problem of precise control of temperatures two requirements were set, in addition to the requirement of accuracy of control. The first was that of reliable operation under any conditions that might be encountered in practice, and the second, minimum attention to maintenance. Both requirements, in the light of our past experience, ruled out the mercury-in-glass or the mercury-in-steel type of regulator. The starting point was therefore a helix of thermostatic metal, similar to that used in the de Khotinsky form of regulator. Although the de Khotinsky regulator is very satisfactory in problems of temperature control where the departure from average may at times be as great as 0.5° C., the standard type did not admit of quite enough precision to hold the temperature of the bath within the A. S. T. M. limits. This is probably due to two difficulties. The first is that in any regulator in which the contacts open and close very slowly, some sticking is unavoidable; second, the presence of dirt on the contact surfaces requires excessive cooling to produce electrical connection at the contact points. Both of these conditions mean departure from average temperature, because at the temperature at which regulation is desired pressure between the contacts is zero. The de Khotinsky regulator fully meets the requirements of ruggedness, and the authors' development was therefore directed toward improving its sensitivity and precision of control. The energy necessary for maintaining such a bath as this at its maximum temperature of 100° C. represents a large current through the contacts—so large that with the mercury thermoregulator a relay would be absolutely essential. When the bimetallic regulator is used, the relay becomes unnecessary, which is an additional reason for choosing this form.

Bad performance of any solid regulator contact is often caused by arcing and burning. A condenser of suitable capacity around the contacts reduces the effect, but the improvement is by no means sufficient to come within the requirements before mentioned. The destructive arc occurs at the break, and only a very slight arc, which apparently does no harm whatever, at the make. It was thought, therefore, that the elimination of the arc at the break would remedy the trouble. Accordingly, a scheme was devised whereby a break at the regulating contacts could never occur. Interruption of the heating current was to be accomplished periodically by a separate mechanism, called the interrupter. To overcome the trouble to be expected from sticking and from dirty contacts, it was decided to have the thermally controlled contact close the circuit on the cylindrical surface of a rotating disk at least as thick as the diameter of the swinging contact. It was decided also that good performance would be insured by providing some means to produce pressure of considerable magnitude between the contacts at the instant they closed.

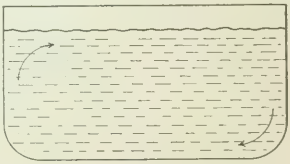

Fig. 1

With these considerations in mind a control circuit as shown in Fig. 2 was outlined. The swinging contact operated by the helix of thermostatic metal was provided with an iron armature, through which was screwed the silver

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[1] Presented before the Section of Petroleum Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Since this paper has been written the authors have designed baths which will accommodate two, four, and six Saybolt tubes, with provision for vigorous circulation of the bath oil.

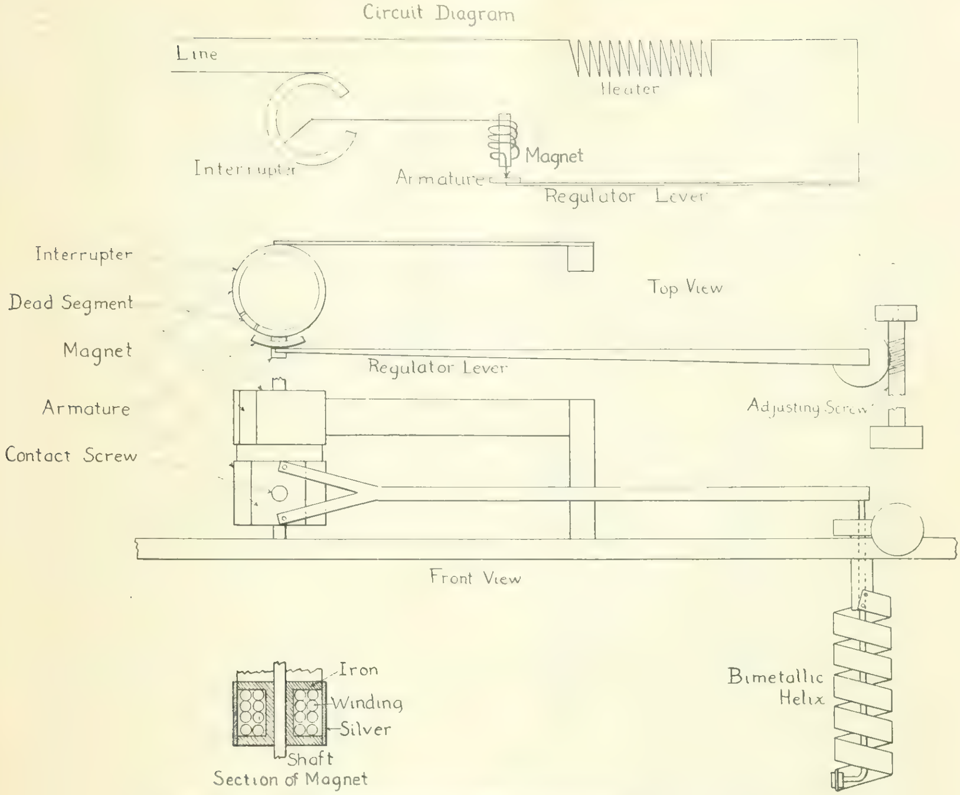

Fig. 2—Bimetallic Thermoregulator with Revolving Contact and Electromagnetic Grip

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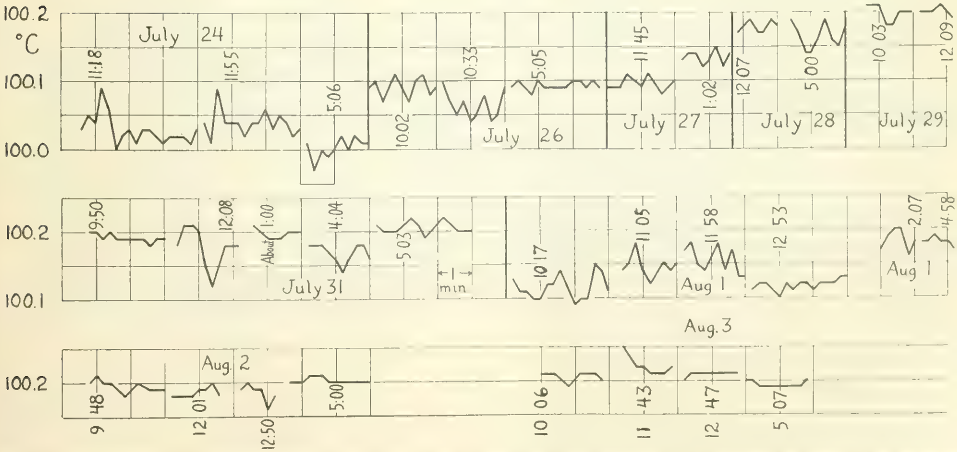

Fig. 3—Readings of Bath Thermometer during 9 Days, during Which the Apparatus Received No Adjustment or Care. The Bath also Operated All Day on July 25, although No Readings Were Taken

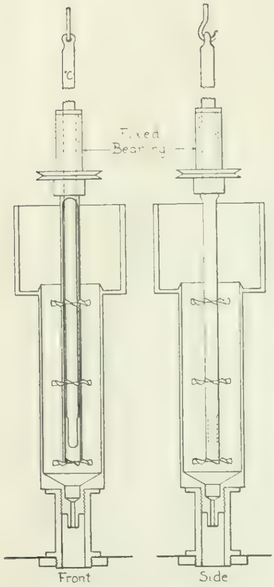

Fig. 4—Stirring by Three Propellers Revolving around Fixed Thermometer

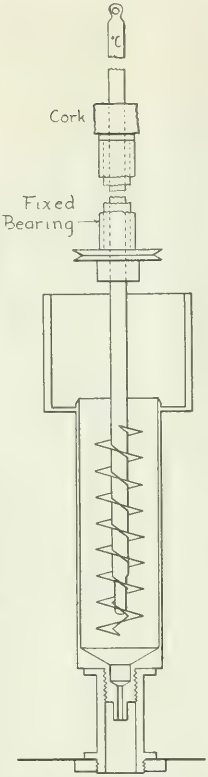

Fig. 5—Stirring by Helix on Revolving Thermometer

contact. In the circuit diagram is shown a magnet so arranged with reference to the armature that when the latter makes contact the magnet is energized by the heating current, thereby producing appreciable pressure at the regulating contact. When the interrupter opens the circuit, this contact is released by the magnet, and separation of contacts will occur if the temperature is above the regulating point, whereas contact persists if the temperature is below the regulating point. Inasmuch as a rotating interrupter has been provided for, it was considered worth while to secure the advantages of the rotating contact and to mount upon the same shaft with the interrupter a continuous silver shell upon which the swinging arm could make contact. The magnet was placed within the silver shell and its construction was such that the attraction of the armature would take place regardless of the angular position of the rotating shaft. The adjustment of the regulator for operation at different temperatures is made in the usual way by slight rotation of the helix. This rotation is accomplished by means of a suitable worm and gear arrangement. A temperature scale is provided by means of which adjustment to within a few degrees of the desired temperature can be made without the aid of a thermometer.

The results obtained with the arrangement just described are best illustrated in Fig. 3. This is a graphic record of readings of the bath thermometer during one period of 9 days, during which the apparatus was in operation 8 hrs. a day without adjustment or care of any kind. The mechanism was in operation on July 25 also, but no readings were taken. Other similar runs were made. Temperatures were observed by means of a thermometer, read to hundredths of a degree. The thermometer was read at 12-sec. intervals over a period of several minutes, and the groups of readings were repeated at the intervals indicated in the graph. During the first 5 days a gradual upward drift was observable, but at the end of that time the automatic control had apparently settled down, so that 100.2° C. was about average temperature. It will be noted that the maximum excursion of the temperature throughout the period in question was 0.28° C., so that the maximum departure from the average was less than 0.2° C. It is also evident that during many minutes and even hours the bath held its temperature within 0.05° C. In this connection it may be mentioned that the sensitivity of the regulator was such that a temperature change of 0.03° C. was sufficient to change the setting of the contact from definitely on to definitely off and vice versa. This figure was determined by repeated tests. The arrangement described therefore accomplishes a very important operation in precise automatic temperature regulation—namely, that the sensitive regulating element retains its sensitivity, but that it makes electrical contact with pressure when temperature change has caused the regulator arm to move into the closed position.

Brief consideration of the mechanism will indicate the reason for the decided advantage of this form of control over any form in which thermal changes alone are depended upon for contact pressure.

Interruption of the circuit takes place periodically, approximately once every 2 sec. Should the bath temperature be higher than the desired point, the contact arm will be in the open position when the interrupter closes, and no heating current will flow until the helix has moved the regulating arm

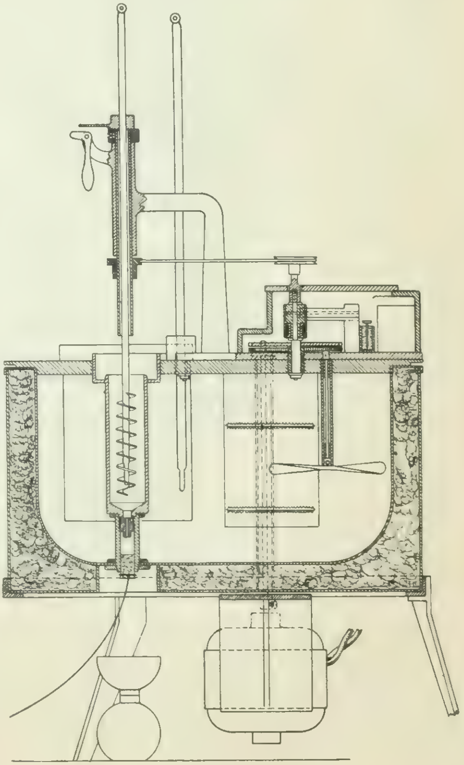

Fig. 6

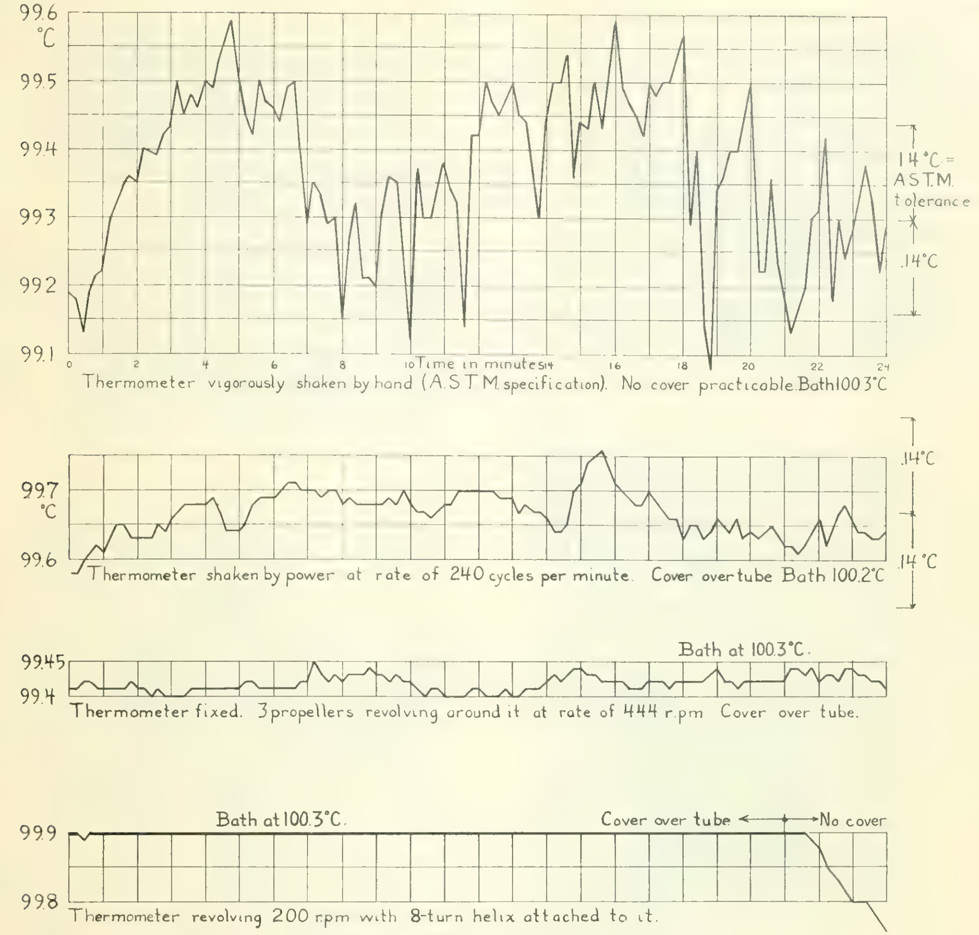

FIG. 7 READINGS OF THERMOMETER IN STANDARD OIL TUBE

into the closed position. Closing of the circuit by the swinging arm may take place at any point on the circumference of the silver shell except the narrow segment corresponding to the insulated segment on the interrupter. If the bath temperature were high, there might be one or several revolutions without contact taking place. On the other hand, if the bath temperature were low, the regulating contacts would be together, and might remain together during a number of revolutions. At regulating temperature the contacts close during each revolution and remain closed through approximately the same arc during each cycle. Should the line voltage increase, the arc of contact would become slightly shorter; should the voltage decrease, the arc of contact automatically would become longer. The same automatic adjustment takes place with changes in room temperature. If the wattage of the heater is increased, the arc of contact will become shorter approximately in the ratio of increase of wattage. This illustrates the flexibility of the arrangement, and it has been found that closeness of regulation (within the limits we chose) is practically unaffected by voltage changes, room temperature changes or changes in the energy input brought about by the condition of the heating units. Whatever the conditions, the regulating helix is permitted to have full control of the situation.

STIRRING DEVICES

Stirring of the oil in the oil tube during the heating process is as important for maintaining constant and uniform temperature in the tube as stirring the oil in the bath, and several methods were tried. Of these the first was to stir the oil in the tube as thoroughly as possible by hand with the thermometer, in accordance with the A. S. T. M. specifications.[3]

The second method of stirring was to mount the thermometer in a swinging bracket, which was moved to and fro by means of the same motor which rotated the propeller and the interrupter.

Another method is illustrated in Fig. 4. The stirrer in this

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[3] The specifications state that "by means of the oil-tube thermometer, the oil in the standard oil tube should be kept well stirred," as should also the oil in the bath.

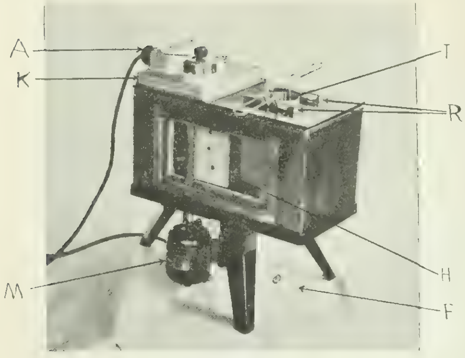

Fig. 8

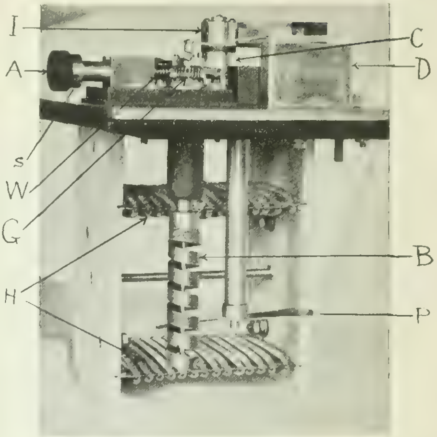

Fig. 10

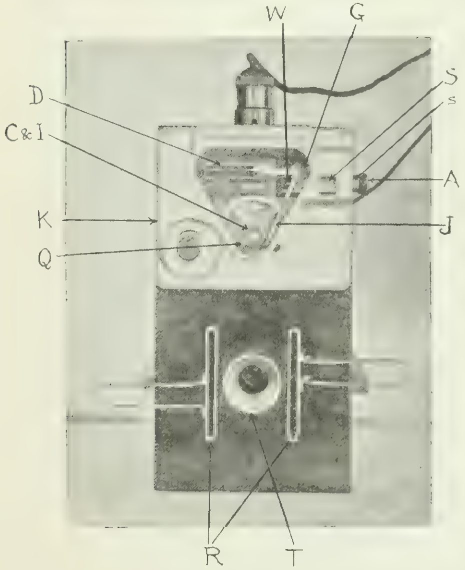

Fig 9

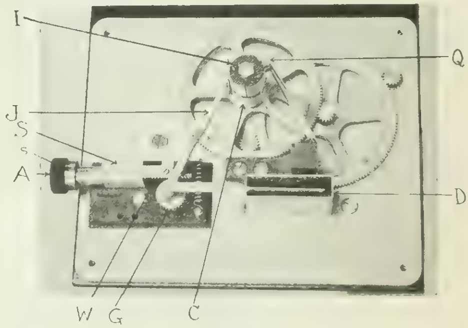

Fig. 11

A, adjusting head of regulator; B, bimetallic helix of regulator; C, cylindrical regulator contact; D, damping box; F, receiving flask; G, worm gear engaging W; H, heating units; I, interrupter; J, thermally controlled contact arm; K, removable cover; M, motor; P, stirring propeller; Q, condenser contacts; R, removable preheating cans for samples; S, coarse temperature scale of regulator; s, fine temperature scale of regulator; T, standard oil tube; W, adjusting worm attached to A.

case was a hollow-shafted propeller with three sets of blades, within which the oil-tube thermometer was placed.

Fig. 5 shows another, and the most successful method. Here the thermometer stem was employed as the stirrer shaft, whereby the large loss of heat by conduction along the metal propeller shaft was avoided. This method consisted merely of slipping a "conveyor screw," made of thin sheet brass, on the lower end of the thermometer, the screw resembling that used in grain conveyors and similar devices.

The results of tests by these different modes of stirring are shown in Fig. 7. All tests there represented were made at 100° C. The A. S. T. M. tolerance at all temperatures is ±0.14° C. Readings were taken at 12-sec. intervals for 24 min. in each case, after it was certain that the temperature equilibrium in the oil tube had been attained. With the method of stirring by hand as vigorously as possible, it is seen that the thermometer readings were quite outside the limits of the A. S. T. M. specifications. In this case a cover on the tube was impracticable. When stirring was effected in the covered tube by means of the thermometer mounted in the swinging bracket, and moved to and fro four times a second, the temperature variations were within the tolerance, although it must be remembered that a thermometer reading is always affected by some lag. Using the hollow-shafted propeller driven at a rate of 450 r. p. m. and keeping the tube covered throughout the interval, the difference between maximum and minimum thermometer readings in a 24-min. interval was 0.05° C. Finally, when the helix on the thermometer was used as the propeller, no variation could be detected on the thermometer so that constancy of 0.01 could be assumed.

Fig. 6 shows a longitudinal cross section of the bath and oil tube with all the accessories in position. Circulation of the oil is downward from the propeller, and the relative positions of propeller and heating coils are such that the heated oil is thoroughly mixed with the cooler portions. This arrangement insures uniformity of temperature throughout the bath. In this figure the conveyor type of stirrer in the oil tube is also shown. The thermometer is held in a hollow rotating shaft by means of a perforated cork stopper resting on the upper end of the shaft. This makes it possible to read the thermometer by merely grasping its upper end. Figs. 8 to 11, inclusive, show the general views of the bath and of the controlling mechanism.

Conclusion

As a result of this investigation the authors conclude that it is possible to hold the temperatures quite within the limits specified by the A. S. T. M., but that properly designed apparatus is required to do so. They believe that the requirement of holding the bath constant "at such a temperature as will maintain the desired temperature in the standard oil tube" is a weak point in the specifications. On account of the great time lag between a change in bath temperature and the effect of such a change upon the oil-tube thermometer, combined with the desire of the operator to lose no time in making the test, it seems likely that in the ordinary procedure there would be considerable lack of agreement between different laboratories running Saybolt viscosity tests on samples of oil from the same barrel. Furthermore, unless the oil in the tube is adequately stirred, the oil-tube thermometer might indicate almost any value within limits wider apart than the A. S. T. M. tolerance. With an apparatus of the kind described, assuming the oil in the tube to be well stirred, the bath temperature can be adjusted until the thermometer in the oil tube shows the desired temperature, and held at this point indefinitely because of the effective control. Although improvement may be possible in the procedure of testing beyond this point, the writers have confined themselves in this work to devise means for meeting the existing requirements.[4]

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[4] Patent application has been filed covering the apparatus herein described and its possible applications.

The Electrical Charge of Vegetable Tannin Particles[1]

By Arthur W. Thomas and Stuart B. Foster

Columbia University, New York, N. Y.

In a previous publication[2] the relation between electrical charge and astringency of vegetable tanning materials was demonstrated, and it was shown that the negative charge of astringent quebracho could be reduced to zero by the addition of hydrochloric acid.

The experiments herein described were undertaken to determine whether the charge could be reversed in sign—i. e., whether vegetable tannins are amphoteric, and, if so, at what hydrogen-ion concentration the reversal in sign of charge takes place. Such data are also needed since Ricevuto[3] has made the quite incredible statement that vegetable tannins are cathodic in migration in alkaline solutions and anodic in acid solutions. He was probably led astray by the fact that his electrodes dipped directly into the tanning solutions and the direction of migration of tannin was interpreted through bulk of precipitate at each electrode upon addition of gelatin. Since Thomas and Frieden[4] have found that gelatin-tannin precipitation depends upon the hydrogen-ion concentration, this may account for Ricevuto's strange findings.

Furthermore, a series of papers by Grasser[5] on electro-osmosis of tan liquors reports variable and somewhat confusing results. Grasser did not determine or control the C_{H^+} of his solutions, and as an unfortunate consequence his data are of very slight practical or theoretical value.

Apparatus

The U-tube electrophoresis method was used to determine the direction of migration of the tannin particles at different hydrogen-ion concentrations.

The U-tube had limbs about 30 cm. long. The bend of the tube was set off from the limbs by stopcocks so placed that the two limbs above them were of equal length. The diameter of the limbs was 1.3 cm. and the bore in the stopcocks was nearly the same width. The electrodes were supported in 30-cc. distilling flasks, the delivery tubes of which had been bent down at right angles and passed through rubber stoppers into the limbs of the U-tube. Small tubes had been blown into the horizontal arms of the two right-angle bends, and were connected by means of rubber tubing and a small stopcock, thus making a salt bridge across the two electrodes.[6] The cathode was a copper wire immersed in a saturated copper sulfate solution, and the anode was a platinum wire in saturated sodium chloride. The source of current was the 120-volt house line, with an electric lamp in series.

Method

The extract solution, previously adjusted to the desired hydrogen-ion concentration by means of the hydrogen electrode, was poured into the U-tube, filling the bend and the bores of the stopcocks. Air bubbles were dislodged, the stopcocks closed, and the limbs, after being rinsed with distilled water, were filled to the brim with a citrate buffer mixture of the same C_{H^+} as the extract in the bend. The flasks containing the electrodes were attached to the U-tube, forcing sufficient of the buffer solution up the delivery tubes and into the flask to complete the conducting circuit. Levels were adjusted through the salt bridge, which was then closed by means of the stopcock. The stopcocks in the limbs were opened carefully and the current was passed until a definite movement of the boundaries was noted.

Considerable experimentation was necessary before a technic was devised which would give consistent results. The first method involved making water solutions of the extracts of such concentration that 100 cc. contained 4 g. of dry solids. It was hoped, of course, that such solutions would really electrophorese—i. e., that the whole column would move toward either the anode or the cathode, according to the C_{H^+} of the extract. But of the six extracts so treated, only one, wattle bark, behaved according to the expectations. Formic acid was then used instead of hydrochloric acid in adjusting the C_{H^+}, and slightly better results were obtained. The final technic, and that upon which the published reports are based, was to dissolve the extracts in citrate buffer mixture at $-\log C_{H^+} = 2.0$, and then adjust the solutions by means of the hydrogen electrode to the exact hydrogen-ion concentration desired. Using the buffer instead of water as the solvent exerted what was apparently a stabilizing effect, and eliminated or delayed the secondary actions, such as diffusion of the boundaries and change of reaction of the extracts due to electrolysis, which behavior had nullified previous experiments.

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[1] Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. Contribution No. 410 from the Chemical Laboratories of Columbia University.

[2] This Journal, **14** (1922), 191.

[3] *Kolloid-Z.*, **3** (1908), 114.

[4] Unpublished.

[5] *Collegium*, **1920**, 17, 49, 277, 332.

[6] Similar to apparatus described by Michaelis, *Biochem. Z.*, **16** (1909), 81.

RESULTS

The table below gives the extracts examined, at the critical hydrogen-ion concentrations, with the corresponding direction of migration of the particles. The extracts were electrophoresed at other C_{H^+}, but only the important data are submitted.

MATERIAL	$-\log C_{H^+}$	DIRECTION OF MIGRATION
Oak	2.0	Cathodic
Oak	2.5	Anodic
Hemlock	2.0	Cathodic
Hemlock	2.5	Anodic
Hemlock	3.0	Anodic
Sumac	2.0	Cathodic
Sumac	2.5	Anodic
Sumac	3.0	Anodic
Quebracho	2.0	Cathodic (?)
Quebracho	2.5	No movement
Quebracho	3.0	No movement
Gambier	2.0	Cathodic
Gambier	2.5	Anodic
Wattle	2.0	Cathodic
Wattle	2.5	Anodic

Quebracho was precipitated by the buffer, hence only the clear supernatant liquid could be used. This fact may account for the inability to obtain positive results.

In all cases the upward movement was slight and frequently was not apparent until the current had been passing from 2 to 3 hrs., but since, with the exceptions noted, there was a corresponding downward movement in the opposite side, the results were taken as conclusive. The method was not susceptible of manipulation sufficiently delicate to permit a determination of the isoelectric points—that is, those hydrogen-ion concentrations where there was movement neither to the anode nor the cathode. However, each of the seven extracts examined (with the possible exception of quebracho) contained positively charged particles at and below $-\log C_{H^+} = 2.0$, and negatively charged particles at and above $-\log C_{H^+} = 2.5$, the isoelectric point or region being between $C_{H^+} = 10^{-2.0}$ and $10^{-2.5}$.

It is stated above that formic acid instead of hydrochloric was employed in certain instances to avoid precipitation of the tannins at high acidities. This is based upon experience of the authors previously published.[2] Since in the earlier work they made no measurements of C_{H^+}, and since they are firmly convinced that no data on the properties of vegetable tannin solutions are of complete ultility unless so controlled, data are submitted herewith relative to the degree of precipitation as a function of the C_{H^+} of acid solutions, and also showing that the nature of the anion of the acid likewise plays a very important role.

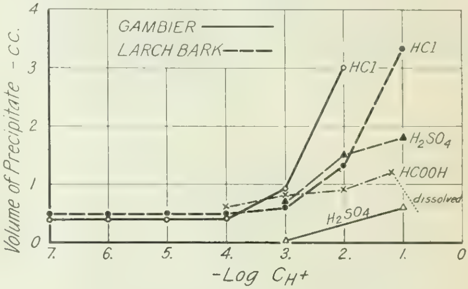
TECHNIC

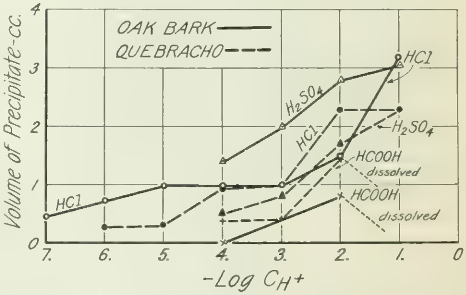
Aqueous dispersions or solutions of the extracts were prepared in the manner described elsewhere.[2] Fifty cubic centimeters of each stock solution were diluted to 100 cc. This dilution was divided into two 50-cc. portions, whose C_{H^+} was then determined with the hydrogen electrode attached to an automatic recorder. The two solutions were adjusted to different C_{H^+} on both the acid and alkaline side of the original C_{H^+}, and the number of cubic centimeters of standard hydrochloric acid or sodium hydroxide solutions required for each point was recorded.

Fifty cubic centimeter portions of the stock solutions were placed in 100-cc. graduated "oil tubes" (tubes tapering to a conical end). The exact quantity of acid or alkali corresponding to a definite C_{H^+} was added and the mixture made up to 100 cc. with distilled water. The tubes were centrifuged for 5 min. at 1000 times gravity, and the volumes of the precipitates were plotted against the hydrogen-ion concentration employed.

RESULTS

The results may be most conveniently studied by examining the curves which show the variation in the amount of precipitate with changes in C_{H^+}. It will be seen that the volume of precipitate, where formed, is not solely a function of the hydrogen-ion concentration, since the three acids gave curves of dissimilar shape.





All the extracts did not precipitate with each acid, and three, sumac, hemlock, and wattle bark, did not give a precipitate with either of the three acids up to $-\log C_{H^+} = 1$. When a precipitate was obtained, the amount invariably increased with increasing hydrogen-ion concentration, where hydrochloric acid or sulfuric acid was used. On the other hand, increasing concentrations of formic acid dissolved the precipitate, or the suspended particles when no precipitate had appeared previously. With decreasing hydrogen-ion concentration there was increasing solution. In every case clear liquids were obtained at $C_{H^+} = 8.0$.

The hydrochloric acid precipitates were found to be soluble in strong alcohol and in 9 *M* lactic acid. On shaking up with water these precipitates dispersed but gradually, and settled out more or less completely in 24 hrs. In the case of oak bark and quebracho it was found that approximately two-thirds of the original solids present had been precipitated at $C_{H^+} = 10^{-1}$.

ACKNOWLEDGMENT

The authors are indebted to A. F. Gallun & Sons Co., of Milwaukee, Wis., for grants in aid of this investigation.

Cerium in Aluminium Alloys[1,2]

By H. W. Gillett[3] and V. H. Schnee[4]

CORNELL UNIVERSITY ITHACA, N. Y.

WORK OF BARTH

IN 1912, Barth,[5] working under Borchers at Aachen, studied the addition of cerium to aluminium. He used aluminium with 0.11 per cent silicon, 0.27 per cent iron, and metallic cerium of 98.34 per cent cerium, containing some silicon and carbon, as well as other rare earth metals, especially didymium. He melted the aluminium in a graphite crucible in a gas furnace, added the cerium, wrapped in aluminium foil, and poured the alloy into an iron mold, casting rods 20 mm. diameter by 300 mm. long which were made into test bars with a breaking section of 15 mm. diameter by 150 mm. long. He gives the following data:

TABLE I—BARTH'S RESULTS

Ce Added %	Ce Found %	Per cent Si	Tensile Strength Kg./Sq. Mm.	Tensile Strength Lbs./Sq. In	Elongation %	Reduction of Area
0	..	0.11	2.86	4080	1.3	3.3
0.05	0.05	0.02	4.00	5700	3.7	3.3
0.10	0.10	0.02	4.87	6950	6.7	6.7
0.20	0.20	0.03	5.52	7850	8.9	10.7
0.40	0.35	0.10	3.86	5500	1.3	2.0
0.60	0.63	0.03	3.71	5270	0.3	2.7
0.80	0.89	0.05	2.67	3800	0.2	2.0
1.00	1.16	0.03	3.29	4680	0.2	3.3
..	8.72	0.06	7.00	9960	0.2	1.3

Notwithstanding the fact that pure chill cast aluminium should give[6] 12,000 to 14,000 lbs./sq. in. tensile strength with at least 15 to 25 per cent elongation, Barth concluded that small amounts of cerium increased the strength and ductility of aluminium. He states that trials in a large aluminium works of an alloy with 0.2 per cent cerium showed no special improvement in tensile strength, but gave 23.6 per cent improvement in ductility. He admits that his test bars were poured too hot.

From his silicon analyses he argues that cerium removes silicon, and postulates that a cerium silicide is formed which is then oxidized, and the cerium oxide is again reduced by aluminium. Just why silicon should be oxidized in preference to aluminium, or should not be reduced when cerium is, is unexplained.

He claims to find, in alloys high in both cerium and silicon, lamellas of some cerium silicide in his micrographs.

Barth does not base his alleged improvements in ductility so much on the removal of silicon as on the removal of gas. He says that his cast pure aluminium rod was solid from top to bottom, while the alloys with cerium were solid at the bottom but had many gas holes in the upper part, which would seem to be an argument against rather than for cerium.

He finds increased corrosion of his cerium alloys in nitric acid as cerium increases, and ascribes this to the presence of a readily soluble silicide. However, he finds a solid solution of cerium in aluminium up to 11 per cent, and, in alloys below 11 per cent cerium, nothing in his micrographs that is due to cerium.

Barth's work and conclusions appear to be of extremely doubtful value.

SCHULTE'S INVESTIGATIONS

In 1921, Schulte,[7] also working under Borchers at Aachen, went into the matter again, stating that subsequent work had thrown doubt on Barth's conclusions. Schulte failed to find a decrease of silicon in the aluminium alloys with cerium, and discards that hypothesis. He found a solid solution and cerium in aluminium up to 13 per cent cerium. He tested rolled material, his results being given in Table II. He does not give the analysis of the cerium used, the analysis of his castings, the size of test bar used, nor the annealing temperatures.

TABLE II—SCHULTE'S RESULTS

Al-Ce Alloys

Annealed[a]

Per cent Ce	0	0.05	0.11	0.19	0.33	0.45	0.77
Tensile strength:							
Kg./sq. mm.	8.63	8.85	8.93	9.1	9.1	9.1	9.15
Lbs./sq. in.	12,250	12,650	12,700	12,900	12,900	12,900	13,050
Elongation, per cent	28.6	30.5	32.4	34.1	34.1	32.6	32.3
Cold worked—Reduction ratio, 70 per cent							
Tensile strength:							
Kg./sq. mm.	15.25	15.4	15.1	14.8	15.0	15.9	16.0
Lbs./sq. in.	21,700	22,000	21,500	20,500	21,500	22,600	22,800
Elongation, per cent	4.6	5.7	6.0	6.4	6.5	6.2	5.1
Cold worked—Reduction ratio, 90 per cent							
Tensile strength:							
Kg./sq. mm.	18.3	..	18.3	18.3	..	18.3	..
Lbs./sq. in.	26,050	..	26,050	26,050	..	26,050	..
Elongation, per cent	1.8	..	3.4	3.7	..	2.9	..

Al-Cu-Ce Alloys—Cu about 3 per cent[b]

Annealed[a]

Per cent Ce	0	0.09	0.19	0.31	0.46
Tensile strength:					
Kg./sq. mm.	17.7	18.0	17.5	17.0	17.0
Lbs./sq. in.	25,200	25,600	24,500	24,200	24,200
Elongation, per cent	24.0	25.0	25.6	22.6	22.0
Cold worked—Reduction ratio 60 per cent					
Tensile strength:					
Kg./sq. mm.	23.0	23.0	23.7	23.9	24.0
Lbs./sq. in.	32,700	32,700	33,700	33,900	34,100
Elongation, per cent	4.0	4.5	5.0	4.0	4.0

Al-Mg-Ce Alloys—Mg about 4 per cent

Annealed[a]

Per cent Ce	0	0.10	0.13	0.16	0.22
Tensile strength:					
Kg./sq. mm.	18.0	19.7	19.9	19.9	...
Lbs./sq. in.	25,500	28,000	28,300	28,300	...
Elongation, per cent	20.0	23.6	22.0	24.0	...
Cold worked—Reduction ratio 60 per cent					
Tensile strength:					
Kg./sq. mm.	37.5	38.8	40.0	40.0	38.4
Lbs./sq. in.	53,000	55,000	57,000	57,000	54,500
Elongation, per cent	2.3	2.3	2.5	3.0	2.3

[a] Control experiments on cast pieces are said to have checked the tensile and elongation figures for these annealed specimens, but no figures are given.
[b] Cast Al-Cu-Ce alloys were not tested.

Schulte claims that the conductivity of aluminium is not decreased by the presence of cerium up to 0.77 per cent. He considers that the alleged improvement in ductility is real, and ascribes it to the elimination of aluminium nitride, stating that his pure aluminium contained 0.028 per cent aluminium nitride, the alloy with 0.2 per cent cerium, 0.014 per cent aluminium nitride, and that with 0.77 per cent cerium, 0.0094 per cent aluminium nitride, but states that "the favorable influence of cerium appears to be strongly encroached upon by the presence of small amounts of other metals." It would have been more convincing if Schulte had given the details of the analytical method for nitrogen, with the data to show how well duplicate samples agreed. On a sample of aluminium that had been overheated and in which the presence of nitrogen was considered possible, one laboratory reported 0.16 per cent and 0.109 per cent aluminium nitride on duplicate samples, while a very careful analyst in another laboratory found in the same samples from 0.02 per cent to 0.012 per cent aluminium nitride.

OTHER PREVIOUS WORK

The curves of Carpenter and Tavernar[8] show that pure aluminium, cold worked and fully annealed, gives 13,000 lbs./sq. in. tensile strength, 36 per cent elongation, while the figures of the Aluminum Company of America[8] show that it gives 13,000 lbs. tensile and 14 to 35 per cent elongation, depending on the gage, and that at a 70 per cent reduction the tensile strength should be 21,000 lbs. and the elongation 2 to 7 per cent, according to gage. At 90 per cent reduction the figures are 30,000 lbs. and up to 2 per cent elongation.

According to the curves of Carpenter and Edwards,[8] a 3 per cent copper alloy, cold rolled, reduction ratio 60 per cent, gives

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[1] Received October 2, 1922.
[2] Published by permission of the Director, U. S. Bureau of Mines.
[3] Chief Alloy Chemist, Bureau of Mines.
[4] Research Engineer, Sibley College.
[5] *Metallurgie*, **8** (1912), 261.
[6] *Bur. Standards, Circ.* **76** (1919), 22.
[7] *Metall u. Erz*, **18** (1921), 236. Translation with comments by "R. E. Search" in *Metal Ind.*, **20** (1922), 142.
[8] Authors quoted in *Bur. Standards, Circ.* **76** (1919), 36, 39, 42. Also recent data from Aluminum Company of America.

40,000 lbs. tensile strength, with about 4 per cent elongation. Hence, while Schulte's alloys containing cerium show, by comparison with his similar alloys free from cerium, a slight increase in ductility, his best figures for the cerium-containing alloys are no better than those given by other authorities for the same alloys free from cerium.

BUREAU OF MINES STUDIES

Considering that the previous results from Aachen obtained by Barth have been discredited, and that the improvement due to cerium alleged by Schulte is pretty small at best, it seemed by no means certain that cerium would be of use in aluminium; but, since the Bureau of Mines, in coöperation with the Welsbach Company, was studying the effect of the cerium group of metals in steel, it was decided to try it out in some cast aluminium alloys also.

EXPERIMENTAL—The aluminium used in making up the alloys contained about 0.25 per cent silicon, 0.25 per cent iron. The cerium-group metals were added as "mix metal." This contained about 10 per cent iron, the balance being cerium-group metals, their proportion being roughly as follows: cerium, 45 per cent; lanthanum, 25 per cent; neodymium and praseodymium, 15 per cent; samarium, 10 per cent. (The word "cerium" in the following description of the Bureau of Mines experiments is to be taken as referring to the mixture of cerium-group elements contained in the mix metal.) The aluminium and rich 50 Cu–50 Al alloy were melted in a rocking furnace. Additions of mix metal or magnesium were made just before pouring into the ladle. Comparison heats were made with and without cerium.

Test bars were cast in green sand in lots of four, and all tensile test figures are the average of four closely agreeing tests. The test bars were of the standard S. A. E. form, tested without machining.

In the 4 and 8 per cent copper alloys, with and without 0.25 per cent cerium equivalent to 0.22 per cent cerium-group metals after deducting iron, which is Schulte's optimum amount of cerium, half of the heat was poured and then the other half heated further to see if cerium would exert its alleged effect on aluminium nitride, whose formation should be facilitated by raising the temperature.

With any alloy used, whether it contained cerium or not, the higher the temperature to which it was heated, the greater the number of pinholes.

DISCUSSION OF RESULTS—The 3.8 per cent Cu, 0.60 Mg alloy was included for comparison with the 3.8 per cent Cu, 0.80 and 1.60 Ce alloys, because magnesium silicide is considered[9] to be in one way or another the active agent in the age-hardening of Duralumin. Merica suggests[10] that it is the removal of free silicon by the formation of the compound magnesium silicide, which is essential. He shows that copper aluminide, which is doubtless the active hardening agent in Duralumin, tends to precipitate about particles of magnesium silicide, which makes it appear that magnesium silicide forms nuclei for the precipitation from solid solution of very finely divided copper aluminide, thus accounting for the necessity for the presence of magnesium in order to secure satisfactory hardening.

If the mere removal of free silicon is the essential point, and if Barth's statement as to the ready formation of cerium silicide is correct—and this is borne out by the statement of Hirsch[11] that in the melting of cerium in a porcelain crucible, the crucible is attacked and a layer of silicide formed inside the crucible which protects it from further attack—it seemed possible that cerium might form cerium silicide, which would act in the same way as magnesium silicide.

But the data of Table III show that it did not, and that the alloys containing cerium were not hardened by the regular heat treatment used on Duralumin.

No signs of any silicide were found on microscopic examination, the alloys with cerium looking just like those without it. In passing, it might be remarked that the heat-treated 3.8 Cu–0.60 Mg alloy did not show, even at 1000 diameters, any of the blue magnesium silicide constituent, but from the solubility curve of Hanson and Gayler[9] no visible magnesium silicide would be expected.

Schulte himself found almost no advantage in the use of cerium in a 3 per cent copper alloy, the elongation on annealed specimens rising from 24.0 to 25.6 per cent and on cold-rolled specimens from 4 to 5 per cent, figures obviously within the variation from bar to bar of such alloys. "R. E. Search," in commenting[7] on Schulte's work, calls this an "important increase" in ductility, and later says that as the weak point of the light aluminium cast alloys is their meager elongation, the "discovery of the increased ductility must be acclaimed as a distinct gain in the fields of endeavor whether purely scientific or practical."

TABLE III -BUREAU OF MINES RESULTS

Cast Cu-Al Alloys

ALLOY Cu Per cent	ALLOY Ce[a] Per cent	Temperature in Ladle °C.	Temperature Poured into Mold	Proportional Limit[b] Lbs./ Sq. In.	Tensile Strength Lbs./ Sq. In.	Elongation Per cent in 2 In.	Brinell (500 Kg.)	Days after Casting before Brinell Test
4	0	700	680	5500	20,000	6		
4	0	760	680	5500	19,200	6		
4	0.25	665	665	5500	19,900	5		
4	0.25	760	680	5500	19,000	4		
8	0	710	680	8500	18,500	1.5		
8	0	810	680	8500	21,000	1.5		
8	0.25	760	680	8500	20,000	1.5		
8	0.25	880	680	8500	19,600	1		
3.8	0	760	670	Not determined	21,000	6.5	43.5	9
3.8	0.80	780	680		17,500	4	42.5	9
3.8	1.60	750	680		17,600	4	41.5	8
3.8	0 0.60 mg.	685	680		21,700	2.5	72	7
6	0	730	680		19,300	3	53.5	8
6	0.80	730	680		19,550	3.5	55.5	8
8	0	740	680		21,700	2.5	65	7
8	0.80	720	680		21,500	2.5	61	7
Heat-Treated Alloys—1 hr. at 495° C. in $NaNO_3$-KNO_3 Quenched in Oil, Heated in Oil 1 Hr. at 145° C.								
3.8	0	760	670	5200	23,100	6.5	45	
3.8	0.80	780	680	5200	19,700	5	40	
3.8	1.60	750	680	5800	22,000	6.5	45	
3.8	0 0.60 mg.	685	680	19,000	31,300	2	76	
6	0	730	680	6600	22,850	2.5	53.5	
6	0.80	730	680	6000	23,800	3	50	
8	0	740	680	6100	22,900	2.5	62	
8	0.80	740	680	6100	21,700	2	55	

[a] "Ce" stands for mix metal, figures not corrected for iron in mix metal.

[b] By Berry strain gage—figure given is point at which slope of stress-strain curve becomes twice that of the elastic portion of the curve.

The results in Table III show, instead, a somewhat decreased ductility, but within the variation to be expected from bar to bar of the alloys without cerium. It should be remembered that the cerium used contained some iron, which increased the iron content of the alloys to which cerium was added so that the iron varied from about 0.25 to about 0.41 per cent and, while no very great effect is likely to be due to this increase in iron, its action would be in the direction of a decrease in ductility.

In the light cast aluminium-copper alloys, whether used in Schulte's optimum amount of about 0.20 per cent or in higher amounts, cerium appears to be without useful effect—in fact, without any marked effect one way or the other.

The possibility still exists that pure cerium, free from the other cerium-group metals, might be of value, but the cost of separation makes that possibility very remote from the commercial point of view, and the chemical similarity of that group of metals makes it rather unlikely that one of them will nullify any benefit caused by another, especially as Schulte's claim is on the basis of scavenging effect on the nitrogen rather than on the basis of true alloying action.

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[9] Hanson and Gayler, *J. Brit. Inst. Metals*, **27** (1921), 321.

[10] Merica, Waltenberg and Scott, *Bur. Standards, Sci. Paper* **347** (1919), 311.

[11] Hirsch, *Trans. Am. Electrochem. Soc.*, **20** (1911), 57.

The aluminium used in the Bureau of Mines experiments was of good quality and probably not contaminated with aluminium nitride. If we accept the unproved assumption that reclaimed boring ingot, for example, does contain aluminium nitride, the possibility remains that a very small "dose" of cerium might help, but it seems certain that in the usual run of good metal used for casting alloys, the use of cerium would be an expense not attended by any benefit.

The test pieces of the Bureau of Mines experiments have not been analyzed. The charges were carefully weighed and there was no sign of loss of cerium. Only cursory microscopic examination of the pieces has been made. In view of the discouraging results of the physical tests it was felt that analytical and micrographic work would be time wasted.

ACKNOWLEDGMENT

Grateful acknowledgment is due to H. S. Miner, of the Welsbach Company, for his coöperation in this work which was done at the joint expense of the Welsbach Company and the Bureau of Mines, under coöperative agreement, to E. Blough of the Aluminum Company of America, for reading the manuscript, and to Cornell University for use of its laboratories and testing facilities.

Contributions to Chemistry of Wood Cellulose
II—Nature of Wood Cellulose[1]

By Louis E. Wise

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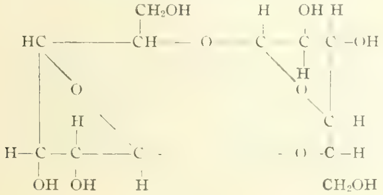
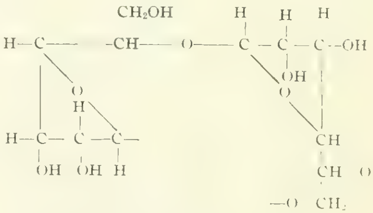
During the World War the dearth of cotton in Germany and Austria stimulated research which had for its object the industrial substitution of wood cellulose for cotton cellulose. It also encouraged comparative studies on the chemical constitution of cotton cellulose on the one hand, and of wood cellulose on the other. The value of such studies is naturally of more than passing academic interest. Their industrial importance may be gaged from a number of articles that have appeared within the past eight years in American and foreign journals of applied chemistry,[2] and the ultimate results of these investigations must have a decided bearing on those industries which require the use of a highly purified cellulose in their manufacturing processes. The accumulation of data, however, gives the industrialist little more than a labyrinth of isolated facts, unless these data are subjected to a thorough critical analysis. Not infrequently such data may be interpreted in a variety of ways, and the danger then arises of accepting an interpretation which will limit or cripple further advance in this particular branch of cellulose chemistry. This article has for its object the brief recapitulation of the experimental work of a number of investigators, the results of which may perhaps be welded into a constructive working hypothesis on the nature of wood cellulose.

CONSTITUTION OF COTTON CELLULOSE

A GENERAL agreement now exists regarding the presence of the cellobiose linkage or residue, or more correctly the anhydrocellobiose linkage, which may be represented by either Formulas I[3] or II:[4]



FORMULA I



FORMULA II

There is at present, however, no definite agreement regarding the limiting yield of cellobiose[4,5] that may be obtained from cotton cellulose. Investigators are by no means in accord when called upon to decide whether or not the cellulose molecule is made up entirely of cellobiose residues.

Different hypotheses regarding the size of the cellulose molecule have also appeared in the cellulose literature. Views on this subject may be briefly summarized as follows: (*a*) a relatively enormous molecule made up of a great number of anhydrodextrose residues,[3,6] many of which go to make up the anhydrocellobiose linkages[7] referred to above; (*b*) a large aggregate made up of comparatively small units, each one of which contains the anhydrocellobiose linkage a relatively small number of times. The units are held together in the larger aggregate by means of secondary valence[8,9,10] or in some similar way which is not yet fully determined. From the work of Herzog and his co-workers[11] it is probable that the cellulose aggregate is crystalline.

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[1] Presented before the Division of Cellulose Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922, in connection with the symposium on "The Nature of Wood Cellulose."

[2] Articles on comparison of wood and cotton cellulose include those by Heuser and Boedeker, *Z angew. Chem.*, **34** (1921), 461; Lenze, Pleus, and Mueller, *J. prakt. Chem.*, **101** (1920), 213; Wise and Russell, THIS JOURNAL, **14** (1922), 285; Mahood and Cable, *Ibid.*, **14** (1922), 727. Articles on nitration of wood cellulose include those by Schwalbe, *Z. angew. Chem.*, **27** (1914), 662; Wells and Edwards, *Paper*, **23** (1919), 180; Woodbridge, THIS JOURNAL, **12** (1920), 380. A modern research on acetylation of wood cellulose is that by Hägglund, Löfman, and Färber, *Cellulosechemie*, **3** (1922), 13.

[3] Hibbert, THIS JOURNAL, **13** (1921), 256; Irvine, *J. Chem. Soc.*, **123** (1923), 525

[4] Karrer, *Helvetica Chim. Acta*, **5** (1922), 187.

[5] Ost, *Ann.*, **398** (1913), 337; Madsen, Dissertation, Hannover, **1917**. Hess and Wittelsbach, *Z. Elektrochem.*, **26** (1920), 232; Freudenberg, *Ber.*, **54** (1921), 767; Irvine, *loc. cit.*

[6] von Euler, *Chem. Ztg.*, **45** (1921), 977, 998.

[7] The older hypotheses, which did not take the cellobiose grouping into consideration, include those of Tollens, "Handbuch der Kohlenhydrate," p. 252; Green and Perkin, *J. Chem. Soc.*, **81** (1906), 811; Cross and Bevan "Cellulose," p. 75; Vignon, *Bull. soc. chim.*, **21** (1899), 599.

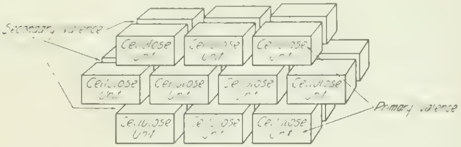

FIG. 1

The viewpoint outlined under (*a*), although still held by individual investigators (like von Euler), has been largely displaced by that referred to under (*b*). Just what the constitution of the individual cellulose unit really is, still forms the subject of extended debates which require no space in this paper. Most investigators are agreed that the cotton-cellulose aggregate is composed of a relatively large number of small units held together by forces which, for the lack of a better name, may be referred to as secondary or auxiliary valences. A crude but rather useful picture of such an hypothesis is given in Fig. 1. The cellulose units may be likened to bricks in a thick wall, the cellulose aggregate. The mortar between these bricks would represent the secondary valence. If the units (bricks) remain undisturbed, but the secondary valence (mortar) is tampered with, changes in state which are so characteristic of cellulose are noted. The individual units or blocks of these units become more or less separated from each other, and a greater surface area is exposed (Fig. 2). Adsorption, which invariably precedes swelling of cellulose, affects the secondary valence. Swelling does not chemically change the little cellulose units; it disturbs the aggregate as a whole.[8] For example, in the swelling caused by the mercerization with alkali, after washing with water, dilute acids (and water), and drying, cellulose shows increased hygroscopicity and an enhanced power of adsorbing substantive dyes, etc. These properties are accounted for in our hypothesis by the increased surface area when the units become partially separated from each other. Hydration due to mechanical beating of cellulose with water, and the first stages in the disintegration of cellulose by means of acids may be similarly explained. Complete peptization of cotton in cuprammonium, zinc chloride, and other so-called cellulose solvents, involves a complete disintegration of the cellulose aggregate, with more or less complete separation of the cellulose units from one another. When cellulose is precipitated in "hydrated" gelatinous form from its sols, the bricks of the original wall are probably in large measure intact. They approach each other, but they no longer present the same orderly arrangement which was manifested in the original cellulose aggregate (wall). This is indicated by the change in crystalline structure in such substances as viscose.[12]

A different picture obtains when the little units themselves become subject to chemical attack. Such attack often follows the partial or complete disintegration of the cellulose aggregate (the wall). It is then that the primary valences within the cellulose units are disturbed. Hydrolysis, acetolysis, and oxidation of cellulose are examples of such attack. Partial hydrolysis—usually referred to under the obscure term "hydrocellulose"—would mean the hydrolysis of a fraction of the number of units originally present in the aggregate. A similar picture would obtain in the case of partially oxidized cellulose (oxycellulose). In either case the hydrolyzed or oxidized material may be adsorbed on the surface of unchanged cellulose units.

In practice these two types of changes cannot be readily distinguished from each other. It is almost impossible to drastically alter a cellulose aggregate, by meddling with secondary valence, without causing some chemical change in at least a few of the cellulose units. When the surface area is increased, the chemical resistance of the unit is weakened. This must be borne in mind in seeking to interpret any analytical data in connection with cellulose. It should also be taken into account when we indulge in the common but rather questionable practice of bolstering our ideas on the constitution of some particular cellulose with a mass of analytical data.

WOOD CELLULOSE

In general, wood cellulose is a residue remaining after more or less drastic treatment of wood to remove lignin and carbohydrates other than cellulose. Such treatment may involve the preparation of chemical pulp by any one of the three well-known processes, or, if the isolation is analytical, may cause the removal of lignin by alternate treatment of the finely divided wood with chlorine and sodium sulfite. In the United States, at least, the term "wood cellulose" has generally referred to the residue isolated by a chlorination method.[13]

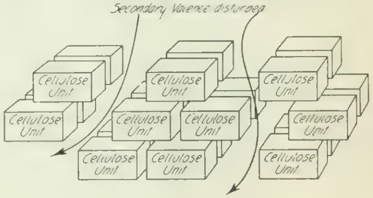

FIG. 2

The residue when subjected to further purification, such as digestion with cold alkali and careful washing with water and acid, has been termed "normal" or "alpha" cellulose. The limitations of these terms have been commented upon in a previous communication.[14] Normal wood cellulose, as defined, possesses the following properties in common with those of cotton cellulose:

1—It may be hydrolyzed almost quantitatively to *d*-glucose. The rate of hydrolysis after peptization of the cellulose is nearly identical with that of cotton cellulose.[15]

2—On acetolysis it yields appreciable quantities of cellobiose octacetate.[16]

3—It shows a crystalline structure practically identical with that of cotton cellulose.[12]

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[8] Karrer, *Helvetica Chim. Acta*, **4** (1921), 811. Karrer, *Cellulosechemie*, **2** (1921), 127.

[9] Esselen, THIS JOURNAL, **12** (1920), 801; see also Minor, *Paper*, **25** (1919), 700.

[10] Hess and Wittelsbach, *loc. cit.*

[11] *Cellulosechemie*, **2** (1921), 101; *Naturwissenschaften*, **8** (1920), 34.

[12] Herzog and Jancke, *Ber.*, **53** (1920), 2126.

[13] Schorger, THIS JOURNAL, **9** (1917), 567; Dore, *Ibid.*, **12** (1920), 266.

[14] Wise and Russell, *loc. cit.*

[15] Heuser and Boedeker, *loc. cit.*

[16] Russell, at the Pittsburgh meeting of the American Chemical Society, reported the formation of cellobiose octacetate on acetolysis of the normal cellulose isolated from each of ten commercial species of wood. Details are reserved for a later publication.

4—On nitration for industrial purposes, it yields nitrates very similar to those of cotton cellulose.[17]

These facts taken by themselves might argue for the identity of cotton and wood cellulose, were it not for the following disconcerting data. Wood cellulose from coniferous woods, even when carefully purified, has been shown by Sherrard and Blanco[18] to yield small but appreciable quantities of mannose on hydrolysis. Wood cellulose isolated from the *angiosperms* when carefully purified still contains small amounts of furfural-yielding substances.[19]

Another argument against the identity of wood and cotton cellulose has been advanced on the basis of the absence of so-called γ-cellulose from purified cotton, and its presence in appreciable quantities in the cellulose obtained from wood.[20]

In the opinion of the writer, however, analytical data regarding γ-cellulose have no vital bearing on the true nature of wood cellulose. The term "γ-cellulose" refers to a fraction, of very uncertain identity, obtained in a convenient but arbitrary analytical procedure, which has never been correlated with problems on the constitution of cellulose. It has been shown that conditions of chlorination influence the amount of α-cellulose very considerably in the same sample of cotton or wood cellulose. Successive chlorinations, while they do not appreciably affect the total cellulose content, serve to decrease the percentage of α-cellulose.[21] This would mean an increase in the β- or γ-cellulose content or in both. It would appear, therefore, that β- and γ-cellulose may actually be considered, in part at least, derivatives of the original cellulose. They may be produced during the chlorination, and are not necessarily part of the original cellulose aggregate. Needless to say, the formation of alkali-soluble cellulose (β- and γ-cellulose) would depend in no small measure on the physical condition (state of aggregation) of the original cellulose. In the case of celluloses which have undergone drastic treatment prior to the cellulose analysis, whether this treatment is due to the action of molds or to a chemical process, lessened resistance to oxidation might be expected, and consequently less α-cellulose and correspondingly more β- and γ-cellulose in the residue after chlorination. In other words, there is at present little or no evidence that β- or γ-cellulose are actually components of the *original material* from which cellulose has been isolated.

The question now arises—can these other data be brought into harmony in the formulation of an hypothesis regarding the constitution of wood cellulose? It must be assumed at the outset that the wood-cellulose aggregate is a very variable one. It is doubtful whether the same investigator can succeed in isolating the same aggregate from the same sample of wood in two successive experiments. This does not mean that the great majority of units in such an aggregate (in purified wood cellulose) may not be identical with the units in cotton cellulose.

If this is true, the minority units—i. e., those *not* identical with the cotton-cellulose unit—which perhaps make up a part of the wood-cellulose aggregate, might reasonably be considered the units of those carbohydrates which are adsorbed on the cellulose during the growth of the cell. Wislicenus and Kleinstuck[22] have shown experimentally that woody tissue is probably built up by adsorption on the cellulose gel of substances derived from the cell sap. This essentially is the process of lignification. The fact that some of these adsorbed substances remain closely associated with the cellulose, even after drastic treatment when so-called typical pentosans, mannans, etc., are dissolved or destroyed by such treatment, is not out of harmony with our general knowledge regarding changes in the properties of substances following adsorption. Purification of wood cellulose always involves the attempted removal of extraneous material with the minimum change in the cellulose. On the other hand, it does not permit the true solution and reprecipitation of cellulose which might facilitate the removal of extraneous material, and it is common knowledge that solids adsorbed by gelatinous precipitates may be exceedingly difficult to remove.

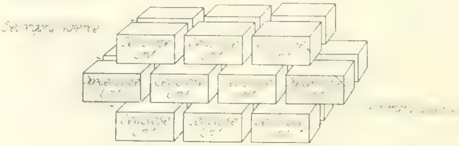

Fig. 3

Taking these facts into consideration, and realizing that cotton and wood cellulose have many chemical properties in common, it appears reasonable to formulate an hypothesis for the structure of wood cellulose which is very similar to that advanced for cotton cellulose. In the case of the wood-cellulose aggregate (the wall), most of the units (bricks) appear to be identical with those in the cotton-cellulose aggregate. Varying amounts, and varying types of other units, however, may also be present in the wood-cellulose aggregate, such units being adsorbed on the surface of the cellulose units during growth. Fig. 3 gives a crude picture of wood cellulose. Again we have the typical cellulose bricks in the cellulose wall held together by secondary valence mortar, but besides we have a smaller number of other units—mannans, pentosans, methyl pentosans, galactans, or any other type of polysaccharide—that can conceivably be adsorbed during the growth of the wall. The number and type of these foreign units depend on the conditions of cell growth and lignification, and also on the purification to which the wood cellulose has been subjected. The hypothesis naturally accounts for any mannose that may be found in the hydrolysis mixtures obtained from the cellulose of coniferous woods. It also explains the presence of furfural and methyl furfural-yielding substances in the α-cellulose isolated from hardwoods.

From such an hypothesis we would expect the purified wood-cellulose aggregate to manifest a behavior similar to that of cotton cellulose in cases where the secondary valences are disturbed. Furthermore, we would expect reactions akin to those of cotton cellulose when wood cellulose is subjected to hydrolysis, oxidation, esterification, and acetolysis. As a matter of fact, the properties of wood cellulose closely approximate those of cotton cellulose, and appear to be in harmony with the hypothesis.

Whereas the foregoing should be taken only as a working hypothesis (and the brick-wall analogy should not be taken too literally), it appears more readily acceptable to the writer than one which admits the possibility of a different cellulose unit for each species of wood. Furthermore, it agrees with the more modern viewpoint on cotton cellulose. Its flexibility is apparent, since it accounts satisfactorily for any percentage of pentosans or hexosans that may be found in the cellulose aggregate. Finally, it seems to harmonize with the present-day concepts of lignification and with the views of plant physiologists and phytochemists.[23]

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[17] Schwalbe, *loc. cit.*

[18] Preliminary reports at the Birmingham and Pittsburgh meetings of the American Chemical Society.

[19] Wise and Russell, unpublished data; also Schorger, *loc. cit.*

[20] Mahood and Cable, *loc. cit.*

[21] Wise and Russell, *loc. cit.*

[22] *Chem. Ind. Kolloide*, **6** (1910), 17, 87.

[23] Wislicenus, *Kolloid-Z.*, **5** (1920), 209.

Distribution of Methoxyl in the Products of Cooking Jack Pine by the Soda Process[1]

By S. S. Aiyar[2]

FOREST PRODUCTS LABORATORY, MADISON, WIS.

This is a continuation of the work on "Distribution of Methoxyl in the Products of Wood Distillation,"[3] and the same general methods were used. Soda cooks on jack pine (Pinus divaricata) were in progress at the Forest Products Laboratory under the direction of S. D. Wells to study the effect of modifications of the process, and it was arranged to procure the necessary samples from each cook to determine the methoxyl distribution.

It was planned to determine methoxyl in the original wood and in the pulp and black liquor as produced under different cooking conditions; the methoxyl in the black liquor was also divided into volatile and nonvolatile.

THE wood, chipped in the usual way, was cooked in a rotary vertical digester with direct and indirect steam heating arrangements. Before starting the cook the chips were impregnated with the caustic lye in the cold at a pressure of 110 lbs. per sq. in., and the liquor was partly withdrawn, leaving behind enough to complete the cook. The lye in the digester was in every case made up to the same strength before turning on steam. As far as possible, all the other factors—viz., concentration of the lye before the cook, amount of caustic on the basis of the wood, time to reach maximum temperature and pressure, weight of wood, etc.—were kept constant. In every cook enough wood to yield 100 lbs. bone-dry wood was used. The only variable was time. The concentration of the lye at the start and of the cooking liquor was kept at about 96 g. per liter in every case.

Samples of white liquor, or caustic lye, were taken before and after impregnation. Steam was then turned on and the cooks started according to fixed schedule. After the prescribed time a sample of black liquor was drawn off through a condenser from each cook and the cook discharged as usual. Samples of pulp were taken after the cooked stocks were washed and pressed.

EXPERIMENTAL

Zeisel's method[4] with the modified apparatus described in the previous paper was used for the determination of the methoxyl in the products. Since the white liquor was repeatedly used to impregnate the wood before cooking, the liquor naturally contained a small amount of methoxyl. This was at no time high, as fresh liquor was added with the consumption of old stock. Yet, an appreciable amount of methoxyl was found to be present in the white liquor both before and after impregnation, and this had to be taken into account in the computations. Knowing the weight of the white liquors introduced and withdrawn, and their methoxyl contents, the required correction could be calculated.

Total methoxyl was determined in one part of the samples of the black liquor and another part was distilled to a thick sirupy residue. The methoxyl was determined in this residue as fixed methoxyl, and the volatile methoxyl of the black liquor was computed by difference.

Duplicates of all determinations were made and the averages of the two, usually varying not more than 0.1 or at most 0.2 per cent, are shown in the tables.

RESULTS AND DISCUSSION

Table I gives the results of the methoxyl determinations on the products of soda cooks of jack pine. It will be seen from the table that not only the methoxy content of the pulp falls as the duration of cook is lengthened, but also the total methoxyl in the pulp based on a constant weight of wood. After 2 hrs. the progressive reduction in both the figures is not so marked as before. In fact, there seems to be no advantage in cooking for longer periods than 2 hrs. from the standpoint of the removal of noncellulose material. Though this is no new fact to the industry, yet it is of interest that it has been brought out by a different procedure.

While the pulp loses methoxyl, the liquor gains it, as would naturally be expected (Table I, Columns 7 and 8). The figures for 4 and 6-hr. cooks need some explanation. The methoxyl content of black liquor of these two cooks seems to be lower than the one above (Column 7), and hence the column, instead of showing an ascending series of figures, shows a fall in the last two figures. This is due to the condensation of a larger amount of water from steam as compared with the 2 and 3-hr. cooks and consequent dilution. There is another discrepancy in both these cooks in that the total methoxyl content of black liquor is above that of wood, which is impossible. There must have been some error in the weight of the black liquor, thus showing a high total methoxyl content. The figures for the 4-hr. cook are especially questionable through all the tables. Even leaving that out of consideration, the conclusions are in no way affected.

It will be seen in Table II that the maximum of the volatile methoxyl compounds is reached in half to one hour after the maximum pressure is attained, and then falls gradually. One would expect that the longer the cook the greater would be the

TABLE I—METHOXYL IN THE PRODUCTS OF SODA COOK OF JACK PINE[a]

1 Duration of Cook from Maximum Pressure Hrs.	2 Dry Pulp from 100 Lbs. Dry Wood Lbs.	3 Weight of Pulp Kg.	4 OCH_3 in Pulp %	5 Total OCH_3 in the Pulp Kg.	6 Weight of Black Liquor after Cook Kg.	7 OCH_3 in Black Liquor %	8 Total OCH_3 in the Black Liquor Kg.	9 Corrections to be Applied for OCH_3 in White Liquor	10 Total OCH_3 in Products Kg.
−0.5	80.7	36.7	4.67	1.714	136.8	0.430	0.59	−0.08	2.22
0	66.5	30.2	3.96	1.196	244.8	0.460	1.127	−0.14	2.18
+0.5	58.4	26.5	3.45	0.914	247.7	0.567	1.40	−0.024	2.3
1	51.6	23.4	2.74	0.64	186.3	0.985	1.83	−0.20	2.3
2	44.6	20.3	1.60	0.33	194.2	0.975	1.89	−0.14	2.10
3	46.0	21.0	1.515	0.32	161.9	1.180	1.92	−0.19	2.10
4	37.1	16.8	1.95	0.33	279.0	0.980	2.70	+0.12	2.90
6	45.7	20.8	1.19	0.24	252.5	0.927	2.34	(b)	2.58

[a] The wood used contained 4.84 per cent methoxyl giving 2.2 kg. methoxyl in each charge.

[b] White liquor samples were not available for the last cook, and hence the correction factor is not known.

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[1] Received December 12, 1922.

[2] Mysore Government Foreign Scholar.

[3] Hawley and Aiyar, THIS JOURNAL, **14** (1922), 1055.

[4] Zeisel, *Monatsh.*, **6**, 989, and **7**, 406.

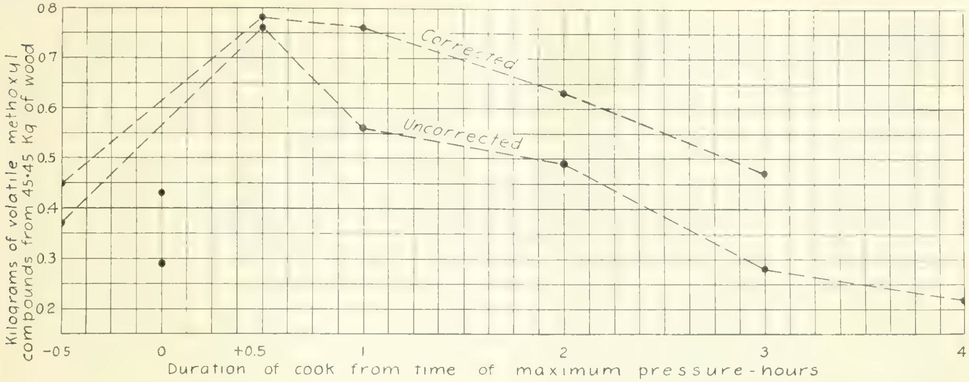

Fig. 1

amount of methanol formed, owing to the hydrolysis of lignin in the wood. But, curiously enough, it seems as though the volatile methoxyl compounds recombine to form stable nonvolatile compounds. The equilibrium seems to be shifted backwards as the concentration of the alkali falls and more woody material is dissolved in the liquor. This reduction cannot be explained by loss of the volatile products, since almost all the methoxyl of the wood is apparently recovered in the products. Although the figures for the last two cooks are questionable, for reasons already mentioned, these conclusions are strongly indicated. Fig. 1 shows this more definitely. According to Bergstrom[5] pine and spruce yield the same amount of methanol in the sulfate process, 15 kg. for 1000 kg. of cellulose manufactured. Five kilograms of this are obtained from the vapors and the rest while concentrating the black liquor. This works out to 1.5 per cent of the cellulose, which is only about 40 per cent of the wood. So, on the basis of wood, the yield of methanol in the sulfate process is not over 0.6 per cent. From small-scale cooks with soda, Bergstrom obtained the following yields of methanol:

	Per cent
Fichte (*Picea excelsa*)	0.67
Kiefer (*Pinus silvestris*)	0.67
Pinus palustris	0.68
Pinus echinata	0.66
Aspen	0.67
Birch	0.81
Gum	0.83

The yield is much less in the case of the sulfite process. The pines, according to the table, yield methanol on an average of 0.67 per cent of the wood. In the work of the authors as much as 1.56 per cent of methoxyl volatile products have been obtained. Of course, this may include not only methanol, but also other volatile methoxyl derivatives. Furthermore, their method of estimation was more quantitative than obtains in the commercial recovery of methanol. The main reason for Bergstrom's low yield is probably that he recovered the methanol after periods of cook longer than one hour, while the author's results show that the volatile products of methoxyl diminish after that period.

In Column 7 of Table II is given a set of figures which represent those in Column 6, corrected for the methoxyl in the liquor introduced for the cook, on the assumption that this methoxyl is fixed. Since this methoxyl is brought into the liquor by its repeated use for impregnation, it may not be far wrong to assume it to be fixed. The fact that the figures in Column 7 show greater regularity than those in Column 6 seems to bear out the assumption. The curves for both corrected and uncorrected figures are given in Fig. 1.

Table II -Fixed and Volatile Methoxyl in the Black Liquor

Duration of Cook from Maximum Pressure Hrs.	Total OCH_3 in Black Liquor Kg.	Residue on Black Liquor %	OCH_3 % of the Residue	Total OCH_3 in Residue (Fixed-Methoxy) Kg.	Volatile OCH_3 Compounds (Diff. of Columns 2 and 5) Uncorrected Kg.	Corrected as per Table I, Column 9 Kg.
−0.5	0.59	19.0	0.86	0.22	0.37	0.45
0	1.13	23.9	1.44	0.84	0.29	0.43
+0.5	1.40	22.9	1.13	0.64	0.76	0.78
1	1.83	32.5	2.10	1.27	0.56	0.76
2	1.89	29.2	2.65	1.50	0.49	0.63
3	1.92	34.7	2.93	1.64	0.28	0.47
4	2.70 (?)	26.7	2.44	1.64	1.06 (?)	0.94 (?)
6	2.34	30.87	2.90	2.26	0.08	(?)

A very interesting relation exists between the lignin and the methoxyl contents of the pulps. Representing these in terms of the percentages based on the lignin and methoxyl in the wood, the figures show a close parallel.

Table III—Relation between Lignin and Methoxyl in the Pulp[a]

Duration of Cook from Maximum Pressure Hrs.	Pulp Obtained in Each Cook %	Lignin in Pulp %	Actual Weight of Lignin Pulp so Obtained Lbs.	Lignin in Pulp on Lignin of Wood %	OCH_3 in Pulp on OCH_3 Content of Wood %
−0.5	80.7	31.7	25.5	80.4	77.9
0	66.5	25.1	16.7	51.4	54.0
+0.5	58.4	23.7	13.9	43.8	41.5
1	51.6	17.4	9.0	28.4	29.1
2	44.6	10.45	4.7	14.8	15.0
3	46.0	10.05	4.6	14.5	14.5
4	37.1	11.9	4.4	13.9	15.0
6	45.7	7.0	4.4	13.9	10.91 (?)

[a] In each cook 100 lbs. dry weight of wood containing 32.8 lbs. of lignin were used.

The last two columns of Table III show this in a striking manner. Allowing for the experimental errors, and more especially for the difficulty in attaining scientific accuracy in the semicommercial cooks on which this study is based, the figures are practically identical. This is in spite of the fact that the methoxyl determinations were conducted by the author and the lignin determination by the Ost and Wilkenung[6] method by Mr. Bray.[7] Hence, there seems to be no doubt that all methoxyl is associated with lignin and that the methoxyl is combined with the lignin in only one way.

Conclusions

As the duration of cook is lengthened the methoxyl in the pulp falls rapidly for the first 2 hrs., and thereafter the methoxy removal is very slow.

The liquor contains volatile and nonvolatile methoxyl compounds, the former attaining a maximum in half to one hour from the time of maximum pressure in the digester. Thereafter, their quantity seems to diminish.

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[5] *Papier-Fabr.*, **10** (1912), 677, 359.

[6] *Chem. Ztg.*, **34** (1910), 461.

[7] Chemist in Forest Products, Pulp and Paper Section of the Forest Products Laboratory.

The lignin and methoxyl contents of pulps from cooks of different duration, expressed in percentages of those of wood are almost identical, thus showing that all the methoxyl is associated with lignin.

This study also shows that there is no advantage in cooking for longer than 2 hrs. at 100 to 110 lbs. per sq. in.

ACKNOWLEDGMENT

The author is indebted to J. A. Staidl and R. H. Grabow for supplying the samples and for all the data on the cooks other than the methoxyl determinations.

Consistency Determination of Greases[1]

By Charles B. Karns and Oscar L. Maag

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WHILE it has been the practice for many years in classifying liquid lubricants to give consideration to their body in determining their value as a specified lubricant in connection with the service requirement, which body or viscosity is determined by instruments available for this purpose, the same cannot be said of solid lubricants such as greases.

For many years greases have been used as lubricants, yet no instrument has been available to determine satisfactorily their consistency or body and thus furnish reliable data as to the general classification of greases for their many different requirements.

The writers with this in mind have spent considerable time in developing a suitable apparatus which will determine accurately the consistency or solidity of not only the soft greases, but the harder solid greases as well. This machine was developed principally for plant control in the manufacture of many kinds of greases, and has been successfully used in this respect for over a year, proving an important factor in the control of grease manufacture, as well as in designating the various grades of greases for general and special lubrication. By means of this apparatus it is possible to classify greases similar to the way that viscosity classifies liquid lubricants such as oils.

The apparatus is so constructed that by pressing a trigger a set of jaws opens and allows a ball of definite weight and diameter to fall a specified distance into the center of a standard cylinder containing the grease to be tested. The depth that the ball penetrates into the grease is measured in millimeters by a depth gage and recorded as the consistency or degree of solidity of the grease.

For lubricants which are too hard to be determined in this manner, such as hard greases for railroad lubrication, the ball falls upon a pin which is held by a disk in the standard cylinder centrally above the sample of hard grease contained in a small cylindrical cup. The depth in millimeters that this pin penetrates into the hard grease is recorded as its consistency. Consistencies determined by the ball falling directly into the grease are denoted by scale S, while readings procured by using the pin are designated by scale H, in order to distinguish results obtained by the two methods.

The tabulated results of consistency determinations of typical greases that cover the hardness ordinarily encountered in these lubricants give an idea of the results obtained with this apparatus.

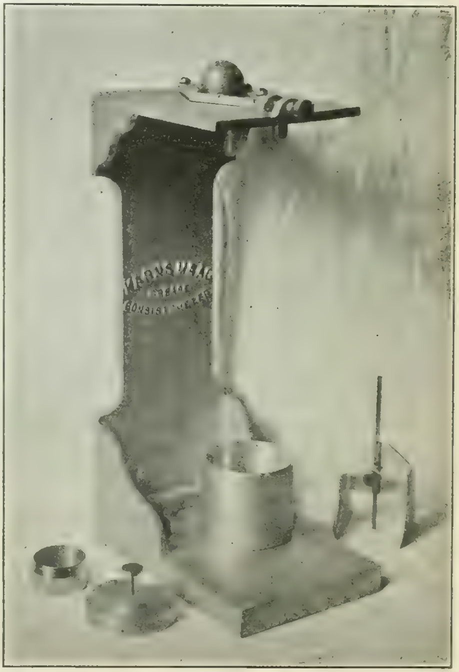
The effect of temperature is quite noticeable on some greases—for example, a soft grease which had a consistency of 35.0, scale S, at 75° F., gave a result of 22.5, scale S, at 35° F. Also, a hard grease, such as used for railroad lubrication, which had a consistency of 7.5, scale H, at 75° F., gave a result of 3.0, scale H, at 35° F.

MOTOR-CUP GREASES	Consistency Taken at 75° F.	
Heavy grade	4.5	Scale S
Medium grade	7.5	
Soft grade	12.5	
Especially soft lubricating grease	35.5	
HARD GREASES FOR RAILROAD LUBRICATION		
No. 1	11.5	Scale H
No. 2	9.0	
No. 3	7.5	

The writers have found the temperature of 75° F. to be very convenient for determining the consistency of most greases; however, for unusually soft greases a temperature of 35° F. is sometimes more satisfactory.

In order that different consistometers may give concordant results it is essential that the parts be thoroughly standardized in their manufacture.

The writers are collecting data with this consistometer relative to the properties of various greases, which they will publish as soon as the work under progress is completed.



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[1] Received December 26, 1922.

The Solvent Properties of Acetone[1]

By R. F. Remler[2]

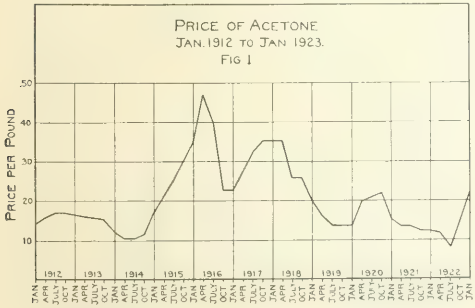
MELLON INSTITUTE OF INDUSTRIAL RESEARCH, PITTSBURGH, PA

Acetone finds wide application in various industries as an organic solvent. Its complete miscibility with water makes it an excellent dehydrating agent, and its miscibility with numerous other solvents permits its use with them, thereby increasing their individual efficiency. In some instances the addition of a small amount of acetone to two immiscible liquids produces a homogeneous solvent.

The purity and uniformity of the present readily available grade of commercial acetone, obtained from calcium acetate, permits its use in processes where the presence of small amounts of foreign substances might interfere with the final product. Its low boiling point enables it to be used for extraction purposes at a low cost for fuel and without danger of decomposition of the final product. Acetone is not as inflammable as benzene, toluene, ethyl ether, petroleum ether, gasoline, or pentane. Its pathological effects are negligible. Its low specific gravity lowers its price per gallon below that of other solvents of higher specific gravity when purchased by the pound. In a number of instances, where used as a lacquer or varnish solvent, its vapors can be recovered by absorption in a suitable medium and then separated by fractionation.

Acetone is used successfully as a solvent for acetylene, cellulose triacetate, cellulose nitrates, celluoid, gums, resins, oils, and fats. Data relative thereto are presented to show the efficiency of the agent.

THE excellent solvent properties of acetone have established its useful application in many industries, notwithstanding the fact that data relative to its value as a solvent are widely disseminated in the literature and are also sometimes indefinite. The large quantities of this solvent used during the World War, in the manufacture of cordite and airplane "dope," exceeded the production from calcium acetate, with the result that new methods for its manufacture were developed. At the present time the supply of the chemical is greater than the demand, and consequently there has been a drop in price (Fig. 1). The availability of acetone in any quantity at a reasonable cost, together with its technically important solvent properties, has suggested consideration to the extension of its present applications and to finding new uses for it in industry. It was for this purpose that the inquiry described in this paper was carried out at the Mellon Institute.


PRICE OF ACETONE
JAN. 1912 TO JAN 1923.
FIG 1

ADVANTAGES OF ACETONE AS A SOLVENT

1—The grade of acetone obtained at present from calcium acetate is of good quality and homogeneity (Fig. 2).

2—It is entirely volatile and does not impart an odor to the solute or extracted material.

3—Acetone has a boiling point of 56.5° C. and freezing point of −94.6° C. at normal pressure.

4—Acetone is inflammable, but not to as great a degree as ethyl ether, carbon disulfide, benzene, toluene, gasoline, petroleum ether, and pentane.[3]

5—Acetone is miscible in all proportions with water and numerous other solvents.

6—It is not only miscible with water, but acts as a "couple" when added to certain immiscible solvents.

7—Acetone is a toxic substance,[4] but its potency is not as great as that of tetrachlorethane, benzene, or methanol.

8—Acetone vapors are recovered easily by absorption in water,[5] cresol and phenols,[6] or wood-tar oil.[7]

TECHNICAL USES OF ACETONE AS A SOLVENT

1—Acetone is not the best but is the most suitable solvent for acetylene.[8]

2—It is one of the most valuable solvents for cellulose esters, especially in connection with smokeless powder and cellulose acetate manufacture.

3—The use of acetone has been proposed for extracting wood pulp,[9] to remove resins and other undesirable material; as a solvent for scrap celluloid in preparing celluloid varnish;[10] as a solvent for celluloid and wax, to prepare an elastic coating for linens,[11] and in making a waterproof adhesive from celluloid and the acetone extract from gum-lac.[12]

4—Acetone is used to a large extent in making paint and varnish removers.[13]

5—Acetone dissolves the lighter constituents from asphalts and bitumens.[14] Wood-tar pitches are more soluble in acetone than in carbon disulfide.[15] Acetone is used as a substitute for benzene-alcohol mixture for extracting montan wax from lignite;[16] for removing paraffin wax from shale oil,[17] and as a solvent in bituminous paints.[18]

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[1] **Presented before the Division of Industrial and Engineering Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.**

[2] **Industrial Fellow.**

[3] Payman, *J. Soc. Chem. Ind.*, **37** (1918), 406R; Fowler, *J. Indian Inst. Sci.*, **4** (1921), 1; Wheeler and Whitaker, *J. Chem. Soc. (London)*, **111** (1917), 267T.

[4] Salant and Kleitman, *J. Pharmacol.*, **19** (1922), 293.

[5] *Rev. prod. chim.*, **23** (1920), 237.

[6] Can. Patent 195,703 (1920); Brit. Patents 127,309 (1917); 128,604 (1917); U. S. Patents 1,315,700 and 1,315,701 (1919).

[7] Brit. Patent 130,962 (1919).

[8] Claude and Hess, *Compt. rend.*, **124** (1896), 626; Butler, *J. Soc. Chem. Ind.*, **40** (1921), 25T; Kremann and Hönel, *Monatsh. Chem.*, **34** (1913), 1089. For solubility of other gases in acetone, *see* Just, *Z. physik. Chem.*, **37** (1901), 342; Stern, *Ibid.*, **81** (1912–13), 468; Levi, *Gazz. chim. ital.*, **31** (1901), ii, 528; McDaniel, *J. Phys. Chem.*, **15** (1911), 587; Ramstedt, *Radium*, **8** (1911), 2536.

[9] Girard, Fr. Patent 443,897 (1912).

[10] Bucheister, *J. Am. Pharm. Assoc.*, **48** (1900), 542.

[11] Friedlander and Tuebben, Brit. Patent 23,547 (1919).

[12] Rampichini, Ger. Patent 253,984 (1911); Brit. Patent 4,253 (1911).

[13] U. S. Patents 725,002; 744,095, 747,898 (1903) 811,044 (1906); 871,790 (1907); 876,251 (1908); 948,814 (1910); 1,035,620; 1,036,946 (1912); 1,051,978 (1913); 1,113,971 (1914); 1,274,430 (1918).

[14] North, *Chem. Met. Eng.*, **26** (1922), 253.

[15] Benson and Davis, THIS JOURNAL, **9** (1917), 141.

[16] Donath, *Breunstoff-Chem.*, **1** (1920), 86; Ger. Patent 342,165 (1918).

[17] Erdman, Brit. Patent 156,594 (1918).

[18] Langfeldt, U. S. Patent 1,397,103 (1921).

6—Acetone is not a rubber solvent and is therefore used in the rubber industry for extracting crude rubber and as a precipitant for reclaiming rubber.[19]

7—Acetone is used in the cleaning industry to remove paint and oil stains.[20]

8—It has been found to be the most suitable solvent for oak tannins.[21]

9—Acetone is employed in the leather industry[22] as a drying or desiccating agent.

10—The use of acetone has been suggested for removing the heavy and high flash point constituents from mineral oils of moderately low specific gravity. It has been shown that oils thus treated give much better service in automobile cylinders.[23]

11—Acetone is also used as a precipitating agent in the preparation of soluble starch.[24]

EXPERIMENTAL

Definite data relative to the solvent properties of acetone for chemical compounds are not available to any great extent in the literature. Naumann,[25] Eidmann,[26] and Krug and McElroy[27] are the main contributors to the solubilities of inorganic salts in acetone. Their results are only relative and in some cases do not agree., As a general rule, however, the bromides, iodides, chlorides, and nitrates are soluble to some extent, while the carbonates, oxides, fluorides, sulfates, sulfites, sulfides, and phosphates are insoluble.

TABLE I—PERCENTAGE OF MATTER IN DIFFERENT RESINS INSOLUBLE IN ACETONE[28]

RESINS	Insoluble in Acetone Per cent
Brazilian	37.60
Zanzibar	77.30
Madagascar	64.30
Demerara	69.20
Columbian	43.60
Benguela	24.80
Angola, red	77.70
Angola, white	61.00
Congo	45.80
Pontianac	Soluble
Kissel	49.50
Akkra	45.80
Cameroon	60.50
Sierra Leone	40.30
Guapinol resin	57.10
Courbaril (Cayenne)	33.90
Manila, hard	52.00
Manila friable, soft	Soluble
Kauri, pale	8.90
Kauri, brown	38.70
Kauri, bush	20.70
Elemi	Soluble
Rosin	Soluble
Burgundy pitch	Soluble
Stockholm tar	Soluble
Dammar (Batavian)	Soluble
Mastic	9.50
Sandarach	Soluble
Madagascar copal, fused	84.80

The solubility data on organic compounds in acetone are decidedly less in number, although more definite, than those reported on inorganic salts, thus leaving an extended field for further investigation. Since acetone is used chiefly as a solvent for commercial products, such as gums, resins, cellulose esters, oils, fats, etc., it seemed that definite data on these could be of value. Most of the results reported on commercial products cover gums and resins, and in many cases these are indefinite; a summary of these data will be found in Table I.

In the experimental determinations of the author on the solubilities of various industrially important products in acetone, the commercial grade of acetone, obtained from the destructive distillation of calcium acetate, was used.[29]

The percentage soluble was determined in most cases by extraction in hot solvent, using the Underwriters' extraction apparatus. The samples were prepared for extraction by covering a wire gauze, rolled in the shape of a cylinder, with the molten sample, or, where heating changed the composition of the product, it was ground and that part extracted which passed through a 20 but not a 60-mesh sieve. In some cases it was necessary to mix the ground sample with previously extracted sand to get complete extraction. Some products, such as rubber, which could neither be ground nor melted, were cut into small pieces and extracted directly. The percentage soluble was calculated by the loss in weight of the sample or by the gain in weight of the flask. The latter method was necessary in some cases, as with crude rubbers, where it was difficult to remove all the acetone from the extracted sample.

OILS, FATS, AND GREASES—Most of the commercial and all the refined vegetable and animal oils tested were miscible in all proportions with acetone at 25° C. In several cases the small percentage of insoluble material was due to some foreign matter. The part soluble at 25° C. was miscible in all proportions. The heavy greases and hydrogenated oils were only partly soluble at 25° C., but were miscible in all proportions at the boiling point of acetone.

FATS, OILS, AND GREASES	Miscibility at 25° C.	Solubility at 25° C. Per cent	Solubility at Boiling Point of Acetone Per cent
China wood oil	M	....	....
Cocoanut oil (refined and bleached)	M	....	....
Corn oil (raw)	M	....	....
Cottonseed oil (refined and bleached)	M	....	....
Cottonseed oil (hydrogenated, Crisco)	M	100.0	M
Cottonseed oil (hydrogenated)	..	32.0	M
Cottonseed oil (stearin)	M	....	....
Cottonseed oil (summer)	M	....	....
Cottonseed oil (winter)	M	....	....
Fish oil (herring, raw)	M	....	....
Fish oil (hydrogenated)	..	35.8	M
Fish oil (menhaden, raw)	*m*	99.8	M
Grease, brown	*m*	96.4	99.8
Grease, garbage	*m*	99.6	99.7
Grease, white	*m*	97.3	M
Linseed oil, raw	M	....	....
Linseed oil, ozonized	M	....	....
Neat's foot oil	*m*	98.7	M
Olive oil (commercial)	M	....	....
Olive Elaine, (red oil)	M	....	....
Palm oil, Legos (commercial)	*m*	82.0	99.8
Palm oil, raw	..	100.0	M
Palm kernel oil (extracted, raw)	M	....	....
Peanut oil (refined and bleached)	M	....	....
Peanut oil (hydrogenated)	..	100.0	M
Pine oil	M	....	....
Seal oil (Norwegian, raw)	M	....	....
Soy-bean oil	M	....	....
Sperm oil	M	....	....
Tallow (prime)	..	89.1	M
Whale oil	M	....	....

M = miscible in all proportions.
m = part soluble at 25° C. is miscible in all proportions.

MINERAL LUBRICATING OILS—Comparative solubility tests were made on a number of mineral oils by adding a small amount of the oil at a time to 100 cc. of acetone, shaking and holding at 25° C. until further addition caused a separation of droplets of oil after standing for some time. The results of these tests are shown in the following table:

OILS	Cc. of Oil Soluble in 100 Cc. of Acetone at 25° C.
Gulf Supreme light auto	13.0
Gulf Supreme medium auto	8.6
Gulf Supreme heavy auto	8.0
Gulf Liberty aero	6.0
Brownley Liberty aero	3.2
High-viscosity pale	6.0
Vacuoline, Extra B	4.2
Turbin	4.2
Western	9.2

It was noted that, as the viscosity of the oil increased, the solubility of the oil in acetone decreased. It is plainly evident, therefore, that acetone is a better solvent for hydrocarbons of low molecular weight, being miscible in all proportions with kerosene, while only 0.209 g. of paraffin is soluble in 100 cc. of acetone at 25° C.[30]

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[19] Zilchert, *Gummi-Ztg.*, **25**, 716; Spence and Scott, *Z. Chem. Ind. Kolloide*, **9** (1911), 83; Stevens, *J. Soc. Chem. Ind.*, **41** (1922), 326T.

[20] Can. Patent 186,251 (1918); *Nat. Cleaner and Dyer*, **13** (1922), 51.

[21] Trimble and Peacock, *Pharm. J.*, **53** (1893), 261, 317; Rau, U. S. Patent 601,170 (1897).

[22] Holland Patent 2,430 (1918); Swedish Patent 41,794 (1917)

[23] Schwarz and Schülter, *Chem. Ztg.*, **35** (1911), 4135. See also Wiederhold, *J. prakt. Chem.*, **47** (1893), 394, for solubility of rosin and mineral oils in acetone.

[24] Fernbach, *Compt. rend.*, **155** (1912), 617.

[25] *Ber.*, **37** (1904), 4328.

[26] Inaugural Dissertation, **1899**, Grefsen, *Chem. Zentr.*, **2** (1899), 1014.

[27] *J. Anal. Appl. Chem.*, **6** (1892), 184.

[28] From Livache and McIntosh, "Manufacture of Varnishes," Vol. 3, p. 115.

[29] This acetone possessed the following characteristics: specific gravity, 0.797 at 15° C.; permanganate test, 60 min.; acidity, CO_2, 0.0014 per cent; alkalinity, nil; residue, nil.

ASPHALTS AND BITUMENS—The following extraction results were had on natural and artificial bitumens:

ASPHALTS AND BITUMENS	Percentage Soluble at Boiling Point of Acetone
Alberite	5.8
Asphalt, blown from midcontinental petroleum	56.4
Bermudez pitch, refined	62.4
Coal-tar pitch, refined	70.4
Fatty acid pitch, soft grade	62.4
Fatty acid pitch, medium grade	54.3
Gilsonite selex	25.0
Grahamite	1.6
Mexican petroleum asphalt, steam-distilled, medium grade	44.2
Mexican petroleum asphalt, steam-distilled, soft grade	64.3
Petroleum asphalt, steam-distilled, California, medium grade	81.0
Residual oil from Gulf Coast	61.0
Residual oil from steam distillation of midcontinental petroleum asphalt	97.2
Syrian asphalt	5.9
Trinidad pitch, refined	42.0

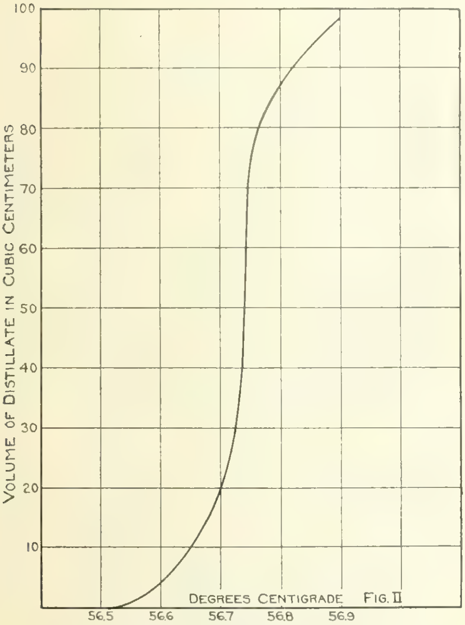

FIG. 2—ACETONE DISTILLATION CURVE

These data support the statement that the solubility of bitumens and asphalts in acetone decreases with increase of hardness. In cases of mineral rubbers or blown asphalts, the acetone-soluble material decreases with the time of blowing, as is shown by the following figures:

TIME OF BLOWING	Acetone Extract Per cent
Residual oil	61.0
After blowing 3 hrs	40.2
After blowing 6 hrs	33.6
After blowing 8 hrs	25.1

ESSENTIAL OILS—The following essential oils were found to be miscible in all proportions with acetone at room temperature:

Anise
Caraway seed
Cinnamon
Cloves
Fennel
Ginger
Limes (distilled)
Orange (sweet)
Pimento
Sassafras
Thyme
Wintergreen (artificial)

RESINS—Of the three different grades of resin tested, the WW grade was entirely soluble in all proportions. The other two grades contained a very small amount of foreign matter insoluble in acetone. The part soluble, however, was miscible in all proportions. The lower melting point coumarone resin tested was entirely soluble and miscible in all proportions with acetone. The higher melting point resin contained a small percentage of insoluble material, which was soluble in concentrate solution but separated out on dilution.

RESINS	Solubility at Room Temperature
Rosin WW grade	M
M grade	*m*
E grade	*m*
Synthetic resins	
Coumarone: m. p. 85° C.	M
m. p. 115° C.	M_1

M = miscible in all proportions.
M_1 = miscible in concentrated solution with part separating on dilution.
m = part soluble is miscible in all proportions at room temperatures.

COPAL RESINS—A number of copal resins were extracted with acetone and the majority contained a large percentage of acetone-soluble matter. In some cases the part soluble was miscible in all proportions, while in others it was miscible only in concentrated solutions, a part separating out on dilution. The results follow:

COPAL RESINS	Percentage Soluble at Boiling Point of Acetone	Solubility of Part Soluble at 25° C.
Congo	40.8	M^1
Manila, soft	96.6	M
Elemi	100.0	M
Yacca	96.6	M
Sandarac	97.0	M_1
Sierra Leone	55.5	M_1
Borneo Pontianac	93.5	M_1
Batavia Dammar	88.7	M_1
Red, accrodites	95.2	M

M = miscible in all proportions.
M_1 = miscible in concentrated solutions with separation on dilution.

WATER GUMS—The solubility of water gums in acetone by extraction is not very great and the part soluble does not form a true solution. Moreover, its solubility at room temperature is not great. The following are the results of extraction tests:

GUMS	Percentage Soluble at Boiling Point of Acetone
Arabic gum	11.9
Indian gum	16.7
Senegal gum	12.0
Tragacanth, Allepa	9.2
Tragacanth, Persian	8.0
Tragacanth, Turkey	7.2

SHELLACS—Acetone is a solvent for shellacs, but does not form a true solution with them. The author found that the best grades of shellacs contained the most acetone-soluble material, and that the solubility per given volume of acetone was increased by the addition of methanol. The results obtained follow:

SHELLAC	Percentage Soluble at Boiling Point of Acetone
Superfine Orange shellac	98.8
Superfine shellac	92.8
T. N. Shellac No. 1	95.6
T. N. Shellac No. 2	98.8
A. C. Garnet	81.3
Refus Lac	63.0

WAXES—The solubility of a number of waxes in acetone at its boiling point showed that the percentage of soluble material decreased with increase in hardness. The softer waxes, as Bayberry, beeswax, and Japan wax, are entirely soluble, while the harder waxes, such as Carnauba and shellac wax, are only partly soluble. Their solubility at room temperature is not very great.

WAXES	Percentage Soluble at Boiling Point of Acetone
Bayberry wax	100.0
Beeswax, African	93.9
Beeswax, Cuban	99.2
Candelilla wax	99.8
Carnauba wax, Flora	35.8
Carnauba wax, Ceara	48.8
Japan wax	100.0
Montan wax	62.5
Ozokerite, black	69.0
Shellac wax	58.8

CELLULOSE ACETATE AND NITRATE—Numerous patents have been granted in the United States and in foreign countries for the use of acetone as a cellulose acetate solvent, both alone and in mixtures with camphor, acetylene tetrachloride, pentachlorethane, chlorinated stearic acid, dichloractone, benzyldihydrocarvone, naphthyl-magnesium halogen compounds, acetyl acetone and ethylidene as solvents and plastifiers. The author found but a small percentage of the cellulose acetate tested insoluble in acetone, the soluble part being miscible in all proportions. The same observation applies to the various grades of cellulose nitrate tested.

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[30] Pawleuski and Filemonowicz, *Ber.*, **21** (1883), 2973.

RUBBERS—A number of rubbers were extracted with acetone and the percentage of acetone-soluble material found in the vaious samples follow.

These figures confirm the statement that acetone is not a rubber solvent, but dissolves only the rubber resins and oils which are found in the better grades of rubbers in amounts less than 5 per cent.

CRUDE RUBBERS	Percentage Soluble at Boiling Point of Acetone
Balata, Surian sheet	41.9
Balata, Venezuela block	44.5
Benguellas	4.5
Caucha Ball	2.9
Caucha, Central	2.8
Crepe, brown	2.8
Crepe, first latex	2.9
Gutta-percha	25.0
Guayale	21.0
Pontianac	95.8
Smoked sheet, primed ribbed	3.15
Upriver Fine	1.25
Upper Congo, red	5.8

Reactions of Accelerators during Vulcanization[1]

V—Dithiocarbamates, Thiuram Disulfides, and the Action of Hydrogen Sulfide

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THE B. F. GOODRICH CO., AKRON, OHIO

Vulcanization has been the subject of careful study by the authors of the present and previous papers on the subject. The present discussion is devoted to dithiocarbamates, thiuram disulfides, and hydrogen sulfide, and their reactions during vulcanization. The conclusions reached are:

Hydrogen sulfide is formed during vulcanization by the action of sulfur on some constituent of the rubber other than the hydrocarbon, and the reaction is accelerated by heat. It decomposes metallic dithiocarbamates, and thus retards or stops curing. The metallic dithiocarbamates may be regenerated by the action of metallic oxides on free dithiocarbamic acid at ordinary temperature. Metallic oxides react with hydrogen sulfide to form sulfides and sulfhydrates, thus protecting dithiocarbamates from decomposition. The shifting of dithiocarbamic acid from one metal to another is due to the intervening action of hydrogen sulfide. Hydrogen sulfide, in the presence of metallic oxides, changes thiuram disulfides into metallic dithiocarbamates. Metallic sulhydrates react with phenyl mustard oil and tetramethylthiuram disulfide to form metallic dithiocarbamates.

In general, the use of a metallic dithiocarbamate with the oxide of another metal gives results comparable with the use of the dithiocarbamate of the metal of the oxide. Lead dithiocarbamates are exceptions. Lead dithiocarbamates, if "protected" by zinc oxide, will accelerate vulcanization without decomposition to lead sulfide. Lead dithiocarbamates act only at relatively high temperatures. Zinc dithiocarbamates function at both high and low temperatures. They are activated by amines but retarded by hydrogen sulfide. Magnesium and calcium dithiocarbamates air-cure more rapidly than the zinc salts, but are less active at higher temperatures. Ammonia gas and other amines form addition products with zinc dithiocarbamates and accelerate curing. Ammonia gas changes thiuram disulfides to dithiocarbamates and thioureas, accelerating air-curing in the presence of zinc oxide.

No evidence has yet been presented contrary to the theory that metallic dithiocarbamates are true accelerators, activating sulfur by the formation of polysulfides whose "super sulfur" is capable of vulcanizing at a low temperature.

HYDROGEN SULFIDE IN VULCANIZATION

TERRY[2] considered the vulcanization of rubber as the substitution of sulfur for hydrogen, but gave no evidence of the formation of hydrogen sulfide, which he postulated. Weber[3] states that not a trace of sulfuretted hydrogen, still less hydrogen, is given off. Schidrowitz[4] says that "the process of vulcanization is not accompanied by the evolution of any appreciable quantity of sulfuretted hydrogen." Later, Weber modified his original statement[5] as follows:

> There is scarcely ever a trace of this gas to be discovered in the rubber works atmosphere* * *. In the vulcanization of hard rubber goods faint but distinct traces of sulfuretted hydrogen are generally, perhaps always, observable, but they could not be ascribed to the vulcanization process proper. Technically pure Para rubber under conditions absolutely precluding the escape of any gaseous product—minute traces of hydrogen sulfide may sometimes be observed * * * with highly purified Para rubber no hydrogen sulfide at all could be detected. If * * * this "insoluble" part of India rubber is mixed with sulfur, and this mixture subjected to vulcanization temperatures, say about 135° C., a considerable evolution of hydrogen sulfide takes place * * * certainly it proceeds much slower than the vulcanization process. The insoluble constitutent of India rubber combines with sulfur under vulcanizing conditions at a very slow rate, with evolution of hydrogen sulfide.

The admirable work of these investigators was directed toward the question of substitution or addition of sulfur with rubber. There is no cause for questioning their conclusions in this respect. Their statements, however, have been the cause of a general impression to the effect that hydrogen sulfide is not formed in rubber stocks during hot vulcanization, and most certainly not at ordinary temperatures. This viewpoint should be corrected since the question of hydrogen sulfide is of vital importance in the study of the mechanism of the action of accelerators. A few observations are therefore recorded which are easily reproducible and which throw new light on the question.

The acetone extract of pale crepe was placed in a test tube with sulfur, under a piece of lead acetate paper held by the stopper. The paper blackened in from 5 to 8 days at room temperature or in 30 to 45 min. in a benzene bath at 80° C.

A mixture of 100 parts rubber and 10 parts sulfur was milled and portions placed in a closed desiccator under lead acetate paper. The paper darkened in from 2 to 4 wks. at room temperature and became black in 2 to 3 mo. The same mix placed under test paper in the bottom of a beaker showed the black color in 2 hrs. on the steam bath or in less than 1 hr. in an oven at 115° C. Test papers scattered around the room proved the atmosphere to be free from hydrogen sulfide. These tests were checked several times with both pale crepe and smoked sheet.

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[1] Presented before the Division of Rubber Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] *J. Soc. Chem Ind.*, **11** (1892), 970.

[3] *Ibid.*, **13** (1894), 1.

[4] Thorpe's Dictionary of Applied Chemistry, **4** (1913), 585.

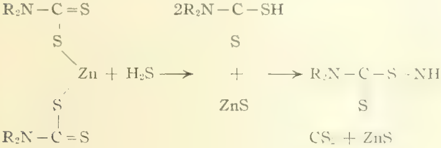
[5] "The Chemistry of Rubber," **1909**, p. 87.

A cement containing only rubber, sulfur, litharge, and solvent will blacken on standing at room temperature.

A mixture of rubber and sulfur slowly evolves hydrogen sulfide at ordinary temperatures, the rate of formation of the gas increasing with rise of temperature.

DITHIOCARBAMATES

Twiss, Brazier, and Thomas[6] describe zinc dithiocarbamates as being almost inactive except in the presence of zinc oxide. The foregoing observations on hydrogen sulfide furnish the explanation of this phenomenon. Hydrogen sulfide precipitates zinc sulfide from solutions of zinc dithiocarbamates, and thereby decomposes the accelerator. This action is the same as that of hydrogen sulfide on zinc acetate or zinc salts of inorganic acids.


(1)

If zinc dithiocarbamates activate sulfur for reaction with rubber, it may be assumed that they also activate sulfur for reaction with rubber resins or proteins whereby the formation of hydrogen sulfide would also be accelerated. This hydrogen sulfide then decomposes the zinc dithiocarbamate and further air-curing of the rubber mix will cease. As a check on this assumption it has been found that air-curing is prevented and heat cures are greatly retarded if stocks containing zinc dithiocarbamates are placed in an atmosphere of hydrogen sulfide for a few hours. The use of from 5 to 10 per cent of zinc dithiocarbamate was then investigated for the purpose of over-riding the effect of hydrogen sulfide. Such a stock, containing no zinc oxide, proceeds to air-cure the same as if zinc oxide and a lower amount of accelerator were used.

TABLE I

Rubber—100, sulfur—5.0, oxide—5.0, $Zn[(S.CS.N(CH_3)_2]_2$—0.3
Press cures 15 min. at 286° F.

	OXIDE	PRESS CURE	AIR CURE	AIR CURE AFTER NH_3
1	None	None	None, 26 days	OK, 11 days
2	ZnO	OK	None, 26 days	OK, 11 days
3	PbO	OK	None, 26 days	None, 26 days
4	MgO	Under	OK, 13 days	OK, 11 days
5	$Ca(OH)_2$	Under	OK, 13 days	OK, 11 days

TABLE II

Same as Table I using $Zn(S.CS.N.C_5H_{10})_2$—0.39

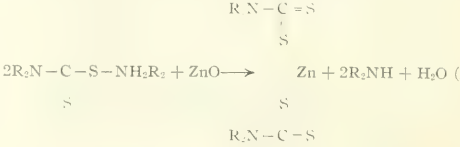
		—PRESS, 286° F.—		
	OXIDE	Min.	Cure	AIR CURE
1	None	15	Under	None, 38 days
2	ZnO	5	OK	OK, 38 days
3	PbO	10	OK	None, 38 days
4	MgO	15	OK	OK, 15 days
5	$Ca(OH)_2$	15	OK	OK, 15 days

In high-temperature cures without zinc oxide an increment of curing power is obtained from zinc dithiocarbamates prior to their decomposition by hydrogen sulfide. Later, the acceleration is produced by the combined action of the decomposition products which consist of amine and carbon disulfide. The cure therefore proceeds the same as if the amine salt of the dithiocarbamic acid had originally been compounded as such, with the exception that more carbon disulfide is now present.

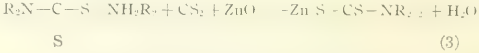
FUNCTION OF ZINC OXIDE

After hydrogen sulfide has decomposed the zinc dithiocarbamate and liberated the amine and carbon disulfide (free dithiocarbamic acid), the action of zinc oxide comes into play and reforms the zinc dithiocarbamate, as shown by the following experiments:

If the amine salt of a dithiocarbamic acid is mixed with zinc oxide and sufficient solvent to moderate the otherwise violent reaction, the zinc salt is at once formed.


$$2R_2N-\underset{S}{C}-S-NH_2R_2+ZnO\longrightarrow \begin{matrix}R_2N-C=S\\ S\\ Zn\\ S\\ R_2N-C-S\end{matrix}+2R_2NH+H_2O \quad (2)$$

If one mol of carbon disulfide is added to one mol of the amine salt, with a further excess of carbon disulfide to moderate the violent reaction, the addition of zinc oxide gives a quantitative yield of the zinc salt with no other reaction product except water.


$$R_2N-\underset{S}{C}-S\cdot NH_2R_2+CS_2+ZnO\longrightarrow Zn(S-CS-NR_2)_2+H_2O \quad (3)$$

A literature search has failed to locate any published description of these two reactions. Primary aromatic amines such as aniline, toluidine, and many others have been found to give violent reactions on mixing with zinc oxide and then adding carbon disulfide. If the temperature is controlled the reaction product will air-cure rubber cements, while if the reaction mixture is allowed to heat up, the odor of mustard oils is very strong and the low-temperature curing power is lost. Neither the cold nor the hot reaction product shows high curing power in heat cures.

By the use of secondary amines such as piperidine or dimethylamine, there is no possibility of a decomposition to mustard oils, and quantitative yields of the zinc dithiocarbamates may be obtained when working with pure materials. Dimethylamine dimethyldithiocarbamate when pure is water-soluble. On standing it slowly develops an increasing water-insoluble content with loss of dimethylamine. One sample went to 40 per cent water-insoluble in 4 mo. This insoluble portion seems to be tetramethylthiuram disulfide. For a study of the reactions shown in Equations 2 and 3, it is therefore necessary to use freshly prepared amine salts. When this precaution is taken, one mol of dimethylamine dimethyldithiocarbamate will react with zinc oxide and carbon disulfide to give a product whose air-dry weight shows the fixing of an additional mol of carbon disulfide, and corresponds to one mol of the zinc salt. An ash analysis of the product gives a zinc oxide residue which corresponds very closely to the formula for the zinc salt.

The need of zinc oxide to bring out the full curing power of zinc dithiocarbamates is for the purpose of maintaining a given concentration of the accelerator in the rubber mix. Hydrogen sulfide is continually destroying the accelerator and zinc oxide is continually reforming the same.

SUBSTITUTES FOR ZINC OXIDE

The reaction of tetramethylthiuram disulfide with hydrogen sulfide to form dithiocarbamic acid has been previously described.[7] If this reaction proceeds as easily as is claimed, the thiuram disulfide should tend to remove hydrogen sulfide from a rubber stock and thereby prevent the decomposition of zinc dithiocarbamates, whereby it might be considered as a substitute for zinc oxide. The following stocks were prepared:

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[6] *J. Soc. Chem. Ind.*, **41** (1922), 81*t*.

[7] Bedford and Sebrell, THIS JOURNAL, **14** (1922), 25.

	A	B	C
Rubber	100	100	100
Sulfur	5	5	5
Zinc salt	0.25	....	0.12
Thiuram	....	0.5	0.25

The third mix, C, was made by mixing the proper proportions of Stocks A and B. These three mixes were cured for 45 min. at 185° F. in an electric oven (open heat). A was barely set or badly undercured; B gave no cure; C gave a snappy overcure.

Tetramethylthiuram disulfide not only protects zinc dimethyldithiocarbamate from decomposition by hydrogen sulfide, thereby acting as a substitute for zinc oxide, but gives the additional effect of free amine on the zinc salt, as will be described subsequently.

TABLE III

Same as Table I using $Pb(S.CS.NC_5H_{10})_2$—0.53

		—PRESS, 286° F.—		
	OXIDE	Min.	Cure	AIR CURE
1	None	15	Under	None, 38 days
2	ZnO	10	OK	None, 38 days
3	PbO	10	OK	None, 38 days
4	MgO	15	OK	None, 38 days
5	$Ca(OH)_2$	15	OK	None, 38 days

TABLE IIIa

Same as Table I using $Pb(S.CS.NC_5H_{10})_2$—0.5

		—PRESS CURES—			—OVEN CURES 185° F.—		
	OXIDE	Min.	° F.	Cure	Min.	Cure	AIR CURE
1	None	15	286	Under	110	None	None, 38 days
2	ZnO	15	260	OK	50	Over	None, 38 days
3	PbO	15	260	OK	50	Over	None, 38 days
4	MgO	15	286	OK	50	Under	None, 38 days
5	$Ca(OH)_2$	15	286	OK	50	Under	None, 38 days

TABLE IV

Same as Table I using $Pb[S.CS.N(CH_3)_2]_2$—0.44

	OXIDE	PRESS CURE 15 min. 286° F.	AIR CURE
1	None	None	None, 75 days
2	ZnO	OK	
3	PbO	Fair	
4	MgO	Under	Under, 13 days
5	$Ca(OH)_2$	Under	

It has also been found that several zinc salts of weak organic acids may be substituted for zinc oxide. To a standard mix consisting of 100 parts rubber, 4 parts sulfur, and 0.5 parts zinc dimethyldithiocarbamate, the following zinc salts were added: (*a*) none (control); (*b*) zinc oxide, 3 parts; (*c*) zinc stearate, 20 parts; (*d*) zinc resinate, 20 parts; (*e*) zinc oxalate, 10 parts; and (*f*) zinc dust (contains ZnO), 20 parts. These six mixes were cured simultaneously in an electric oven for 30 min. at 215° F., with results as follows: (*a*) no cure, (*b*) and (*c*) snappy overcure, (*d*) and (*e*) fair cure, and (*f*) snappy overcure.

Further experiments show that zinc soaps will react with dimethylamine dimethyldithiocarbamate in carbon disulfide to form the zinc dithiocarbamates and free fatty acid. Zinc salts of weak acids, therefore, act in the same manner as zinc oxide and remove hydrogen sulfide or reform zinc dithiocarbamates after they have been decomposed by hydrogen sulfide. The oxygen of zinc oxide is nonessential; it is the zinc radical which is effective.

TRUE ACCELERATORS

Further evidence that the metallic dithiocarbamates are true accelerators is found in the action of lead dithiocarbamates. Zinc oxide, when used with this accelerator, apparently reacts with hydrogen sulfide direct, thereby protecting the lead salt from decomposition. A mix consisting of: rubber, 100; sulfur, 5; zinc oxide, 10; and lead dimethyldithiocarbamate 0.5 will cure in 45 min. at 185° F. without turning black. In the absence of zinc oxide, lead sulfide is formed and no cure results.

If dry hydrogen sulfide is passed over zinc oxide at room temperature, the oxide becomes hot, water is liberated, and zinc sulfide is formed. A quantitative yield of zinc sulfide is not obtained by this reaction of powder with gas which seems to show only a superficial action of hydrogen sulfide on the zinc oxide crystals. The action of hydrogen sulfide on litharge and calcium hydroxide at ordinary temperatures is well known. With zinc oxide it was believed that further laboratory tests were necessary to show its rapid reaction with hydrogen sulfide. Hydrogen sulfide also reacts rapidly with zinc oxalate and zinc soaps.

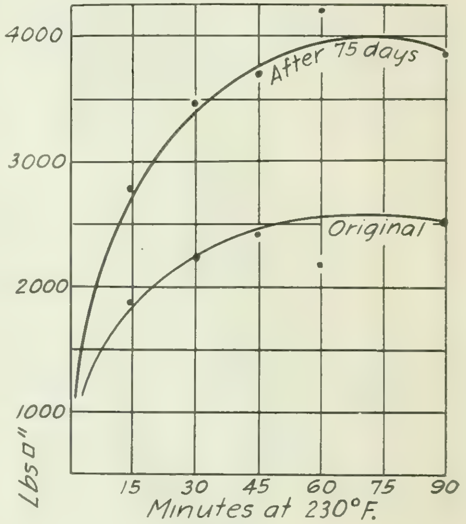


FIG. 1

Zinc compounds, therefore, may act as secondary accelerators to metallic dithiocarbamates in two different ways.

(1) They may react with hydrogen sulfide and thereby protect the primary accelerator from decomposition.

(2) They may reform the accelerator after it has once been decomposed. The ultimate effect by either method is the same.

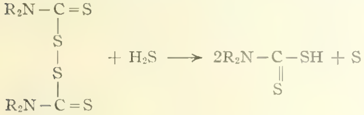
TIME FACTOR AND MASS ACTION

The theory of decomposition of a zinc dithiocarbamate by hydrogen sulfide and its re-formation by reaction with zinc oxide requires the migration of the free amine and carbon disulfide (dithiocarbamic acid) from the place in the rubber mix where the zinc salt was decomposed to the location of a particle of zinc oxide. Zinc oxide, *as such*, is not in solution in rubber, and therefore cannot migrate by diffusion. The free dithiocarbamic acid must therefore diffuse to the zinc oxide particle. With large amounts of zinc oxide distributed through a rubber stock, its action may be chiefly the removal of hydrogen sulfide. With high amounts of accelerator and high zinc oxide, the decomposed accelerator will find plenty of fresh zinc oxide in its immediate vicinity and the zinc salt will reform at once. Low accelerator and low zinc oxide, however, present an entirely different set of conditions. In such a stock the condition might easily arise where a large portion of or all the zinc dithiocarbamate had been decomposed and had not yet migrated to the location of unreacted zinc oxide. Such a stock would tend to show a flat curing curve, and yet after removal from the press might proceed to air-cure further on standing where time would allow migration and re-formation of the zinc salt.

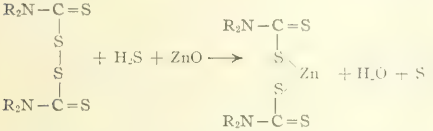
Many instances of this phenomenon have been found, as illustrated by cures on a stock containing: rubber, 100; zinc oxide, 5; sulfur, 2; and zinc dimethyldithiocarbamate, 0.2. The original tensiles are shown by the lower curve in Fig. 1. The same sheets from which the tensile pieces were cut were placed in a dark cabinet and stored for 75 days at room temperature. They were then retested, with the results shown in the upper curve. The question of equilibrium is, therefore, an important one in the study of the action of accelerators, and where mass action is low the time factor seems to dominate.

THIURAM DISULFIDE

The action of hydrogen sulfide on tetramethylthiuram disulfide[7] forms free dithiocarbamic acid, which then reacts with zinc compounds to form zinc dithiocarbamates.



$$\begin{array}{c} R_2N-C=S \\ | \\ S \\ | \\ S \\ | \\ R_2N-C=S \end{array} + H_2S \longrightarrow 2R_2N-\underset{\underset{S}{\|}}{C}-SH + S \qquad (4)$$



$$\begin{array}{c} R_2N-C=S \\ | \\ S \\ | \\ S \\ | \\ R_2N-C=S \end{array} + H_2S + ZnO \longrightarrow \begin{array}{c} R_2N-C=S \\ | \\ S \\ \quad\searrow \\ \qquad Zn \\ \quad\nearrow \\ S \\ | \\ R_2N-C=S \end{array} + H_2O + S \qquad (5)$$

This reaction in rubber has been studied in the light of recent developments. The liberation of sulfur according to Equation 4 has not vulcanized rubber cements. In a zinc oxide-rubber-sulfur cement or dry stock a small amount of hydrogen sulfide will cause air-curing with tetramethylthiuram disulfide. A large excess of hydrogen sulfide decomposes the zinc dithiocarbamates which are formed, reacts with the available zinc oxide, and prevents air cures. Organic softeners, such as pitches, oils, resins, etc., often show a retarding action. This is attributed to the increase of hydrogen sulfide resulting from their reaction with sulfur.

TABLE V

Same as Table I using $Mg(S.CS.NC_5H_{10})_2$—0.5

	OXIDE	PRESS CURE Min.	PRESS CURE ° F.	PRESS CURE Cure	OVEN CURES, 185° F. Min.	OVEN CURES, 185° F. Cure	AIR CURE
1	None	15	286	Under	110	Under	None, 38 days
2	ZnO	8	240	OK	20	OK	Under, 5 days
3	PbO	15	260	Fair	50	Fair	None, 38 days
4	MgO	15	286	OK	50	Under	None, 38 days
5	$Ca(OH)_2$	15	260	OK	50	Under	Under, 12 days

TABLE VI

Same as Table I using $Ca(S.CS.NC_5H_{10})_2$—0.5

	OXIDE	PRESS CURE Min.	PRESS CURE ° F.	PRESS CURE Cure	OVEN CURES, 185° F. Min.	OVEN CURES, 185° F. Cure
1	None	15	286	Under	110	Under
2	ZnO	8	240	OK	20	OK
3	PbO	15	260	OK	50	OK
4	MgO	15	286	OK	110	Under
5	$Ca(OH)_2$	15	260	OK	110	Under

TABLE VII

Same as Table I using $(CH_3)_2NH_2.S.CS.N(CH_3)_2$—0.33

	OXIDE	PRESS CURE Min.	PRESS CURE ° F.	PRESS CURE Cure	AIR CURE
1	None	15	286	Under	None, 75 days
2	ZnO	15	230	OK	OK, 13 days
3	PbO	15	286	OK	None, 13 days
4	MgO	15	286	Under	OK, 13 days
5	$Ca(OH)_2$	15	286	Under	OK, 13 days.

Litharge reacts so readily with hydrogen sulfide to form lead sulfide that it might be expected to prevent the action of this gas on thiuram disulfides and thereby retard the action of such accelerators. A laboratory study of these reactions shows that this is not the case.

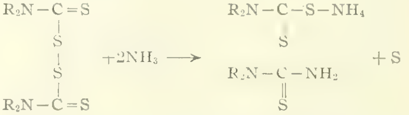
Hydrogen sulfide, when passed into a rubber-sulfur cement containing litharge, produces at once black lead sulfide. If the cement is chilled, the red color of the lead sulfhydrate is first developed, changing shortly to black. On the addition of tetramethylthiuram disulfide to the cement, the action of hydrogen sulfide first shows the red sulfhydrate color which, instead of turning black, changes to white or gray, and no lead sulfide is formed until either the litharge or the thiuram is nearly all reacted upon. A rapid stream of gas will give black sulfides at once, but a slow stream with stirring gives the results described. Lead dimethyldithiocarbamate is formed.

The same action is found with phenyl mustard oil and litharge on passing in hydrogen sulfide. The lead salt of phenyl dithiocarbamic acid is formed. The low curing power of phenyl mustard oil as found by Twiss[8] is therefore probably due to the formation of a small amount of the zinc salt of phenyl dithiocarbamic acid. Bruni's reaction[9] of phenyl mustard oil with sulfur to form mercapto benzothiazol does not take place as easily at the temperature of 138° C., used by Twiss, as the reaction of sulfur on rubber resins (or proteins) to produce hydrogen sulfide.

The presence of metallic oxides aids, rather than prevents, the formation of dithiocarbamates by the action of hydrogen sulfide on tetramethylthiuram disulfide.

ACTION OF AMMONIA AND AMINES

Fromm[10] shows that ammonia, aniline, and other amines easily react with disulfides which have a double bond adjacent to the $\equiv C-S-S-C\equiv$ group, such as tetramethylthiuram disulfide, according to the following equation:



$$\begin{array}{c} R_2N-C=S \\ | \\ S \\ | \\ S \\ | \\ R_2N-C=S \end{array} + 2NH_3 \longrightarrow \begin{array}{c} R_2N-\underset{S}{C}-S-NH_4 \\ \\ R_2N-\underset{\underset{S}{\|}}{C}-NH_2 \end{array} + S \qquad (6)$$

Cadwell[11] uses aniline with thiuram disulfides, dithiobenzoyl disulfide, metallic xanthogenates, etc., to induce rapid air cures in the presence of zinc oxide. In Tables IX and X it is shown that ammonia has the same effect on the cure, by reaction with thiuram disulfides to produce dithiocarbamic acids, which in turn form zinc salts by reacting with zinc oxide.

The action of ammonia on thiuram disulfides does not stop with the formation of the zinc dithiocarbamates. Bedford and Sebrell[7] noted the accelerating action of aniline on zinc dithiocarbamates, but were somewhat in doubt as to whether the rapid air-curing was due to other than the solvent action of aniline for the zinc salt. Ammonia has the same effect as aniline. A zinc dithiocarbamate of a secondary amine air-cures far more rapidly after the dry stock has been kept over night in an atmosphere of dry ammonia gas. The stock is then exposed to air and kept at room temperature. The effect of ammonia cannot be due to solvent action. It is evidently connected with the formation of an additive reaction product with the zinc dithiocarbamate.

Dry ammonia gas was passed upward through a cylinder containing one mol (305 g.) of zinc dimethyl dithiocarbamate. An exothermic reaction took place. The cylinder was allowed to cool before the flow of gas was interrupted, and the contents were then spread out in air to remove all odor of ammonia.

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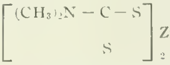
[8] *J. Soc. Chem. Ind.*, **40** (1921), 242*t*.

[9] *Giorn. chim. ind. applicata*, **3** (1921), 351; *C. A.*, **15** (1921), 3915.

[10] *Ann.*, **348** (1906), 144.

[11] Brit. Patent Application 174,915 (1922).

The weight increase was 17 g. or the equivalent of 1 mol of ammonia. The formula of the new compound probably is



$$\left[\begin{array}{c}(CH_3)_2N-\underset{\displaystyle S}{\overset{\|}{C}}-S\end{array}\right]_2 Zn.NH_3$$

Lead dithiocarbamates do not give addition products with ammonia, nor does ammonia cause them to air-cure.

TABLE VIII

Same as Table I using $C_5H_{10}NH_2.S.CS.NC_5H_{10}$—0.49

		PRESS CURE			
	OXIDE	Min.	° F	Cure	AIR CURE
1	None	15	286	Under	None, 75 days
2	ZnO	15	230	OK	OK, 13 days
3	PbO	15	286	OK	None, 13 days
4	MgO	15	286	Under	OK, 13 days
5	$Ca(OH)_2$	15	286	Under	OK, 13 days

TABLE IX

Rubber 100, sulfur—4.0, oxide 0.5, tetramethylthiuram disulfide—0.25

	OXIDE	PRESS CURE 15 min., 260° F.	OVEN CURE 50 min., 176° F. As is	After NH_3	AIR CURE As is	After NH_3
1	..	.....			.	
2	ZnO	Over	None	Over	None	Fair, 8 days
3	PbO	Under	None	None	None	None
4	MgO	Under	None	Under	None	None
5	$Ca(OH)_2$	Fair	None	Under	Good, 8 days	Good, 8 days

TABLE X

Rubber—100; MgO 0.5; tetramethylthiuram disulfide—0.5

SULFUR	PRESS CURE 5 min., 240° F.	AIR CURE As is	After NH_3
4.0	Under	OK, 50 days	OK, 13 days
6.0	Fair	OK, 34 days	OK, 13 days
8.0	OK	Over, 27 days	OK, 13 days

RELATIVE ACTION OF VARIOUS OXIDES

The idea of continual decomposition and re-formation of metallic dithiocarbamates during vulcanization at once suggests a possibility of the shifting from one metallic salt to that of another metal. Upon studying the action of various oxides on a certain metallic dithiocarbamate, their action was found to be so widely different that the results could be recorded qualitatively by the feel of the cured vulcanizate. Considering acceleration purely as a time factor, the relative action of the common oxides has been recorded through the time necessary to give an under, fair, OK, or over cure. This was partly necessary in order to correlate air cures properly with press or oven cures, since, air cures do not lend themselves readily to machine tests.

The treatment with ammonia gas consisted merely of exposing the stocks, in thicknesses not over 0.25 in., to the dry gas over night at atmospheric pressure, or for shorter periods when using higher pressure. All stocks were then exposed to air for at least one day before being cured in press or oven.

The entire data are given in Tables I to X.

DISCUSSION OF DATA

From the foregoing data it was found that lead dithiocarbamates do not air-cure except by the aid of calcium hydroxide or magnesia, and then but slowly. The lead salts are high-temperature accelerators and require the presence of litharge or zinc oxide. Litharge used as an aid to the dithiocarbamates of zinc, calcium, or magnesium gives practically the same results as if the lead salt had been used.

Zinc dithiocarbamates air-cure most rapidly with calcium hydroxide and magnesia, more slowly with zinc oxide, and not at all in the presence of litharge. For high-temperature cures calcium hydroxide and magnesia lose their value and become secondary to zinc oxide and litharge. In each case the resultant cure corresponds closely to that of the metallic salt of the oxide used.

Calcium and magnesium dithiocarbamates of secondary amines are rather unstable, decomposing with rising temperature and thereby losing the high curing power which they show at ordinary temperatures. When used with zinc oxide or litharge they assume the properties of the zinc or lead salts.

Ammonia causes zinc dithiocarbamates of secondary amines to air-cure in absence of metallic oxides so that they function as rapidly as by the aid of calcium hydroxide or magnesia. The ammonia is believed to be held as an addition product to the zinc salts, and probably increases the basicity of the accelerator, thereby giving greater curing power. With thiuram disulfides the ammonia first forms the corresponding dithiocarbamate.

The data check the previous assumptions and show the shifting from one metallic salt to another during vulcanization. This is believed to be due to the interfering action of hydrogen sulfide. Metallic oxides apparently do not fix hydrogen sulfide sufficiently to prevent the interchange of metallic radicals. Litharge stops the zinc salt from air-curing and magnesia speeds its action. Lead and magnesium sulfhydrates evidently react with zinc dithiocarbamates to form lead or magnesium salts and precipitate the zinc as the sulfide. It will be recalled that litharge does not prevent the action of hydrogen sulfide on thiuram disulfides.

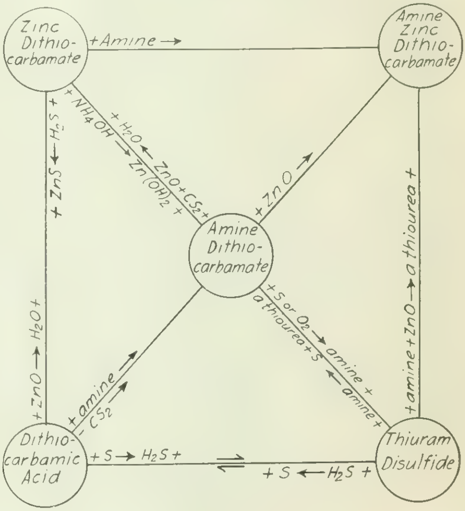


FIG. 2

In conclusion, there is shown in Fig. 2 a graphical outline of the many reactions which take place with dithiocarbamates and thiuram disulfides derived from secondary amines. All these reactions take place at room temperature.

Nitrostarch as a Constituent of Explosives

The use of nitrostarch in the manufacture of safety explosives is increasing, and this substance is now important in the explosives industry, state C. A. Taylor and W. H. Rinkenbach, assistant explosives chemists of the Interior Department, who have conducted a series of studies of the materials, constitution, and analysis of numerous types of explosives at the Pittsburgh Experiment Station of the Bureau of Mines. Nitrostarch is made by nitrating starches with a mixture of sulfuric acid and nitric acid, details of the method varying considerably among different manufacturers. Commercial nitrostarch is in reality a mixture of compounds of various degrees of nitration, being comparable in this respect with nitrocellulose. Like the nitrocellulose, nitrostarch is not a true nitro compound, being an organic nitrate.

Limitations of the Obscuring Power Method of Determining the Particle Size of Pigments[1]

By Ellwood B. Spear and Herbert A. Endres

The Goodyear Tire and Rubber Co., Akron, Ohio

A critical study of the obscuring power method for determining the relative average particle size of pigments has been made.

The method is applicable for comparisons of particle size of the same pigment in the same medium where the average diameter of the particles is greater than one-half the wave length of light. It serves as a convenient and rapid check on the physical condition of two shipments of the same material produced by the same process even when the average diameter of the particles is somewhat less than one-half the wave length of light.

The method, however, is not applicable for the comparison of two different pigments if an appreciable difference exists between their respective refractive indices, or other optical properties, such as light absorption and reflection. For instance, zinc oxide and gas black will not give the same obscuring power values, even if the average diameter of the particles is the same in the two cases. It is not applicable for the determination of particle size in systems where the diameter of the particles is less than one-fourth the wave length of the light employed—i. e., in colloidal systems.

THE so-called obscuring or diffusing power test is a turbimetric method of determining the average particle size of pigments, and has been previously described in the literature.[2,3] The fundamental principle of the method is the extinction, partly by absorption, partly by scattering, due both to refraction and reflection, of the direct light rays from the incandescent filaments of an electric lamp caused by the dispersed pigment particles in the tube through which the lamp is viewed. The chief factors involved are the size of the particles, the difference of refractive indices of the dispersed material and the disperse medium, the absorption of light by the particles or by the medium, and also reflection from particles, depending upon the angle presented to any ray. The importance of the difference of refractive indices of the dispersed phase and dispersing medium should be stressed, because if both phases have the same refractive index there will be neither refraction nor reflection and the system will appear homogeneous and entirely transparent. Obviously, in this case an obscuring power reading could not be obtained.

The apparatus employed is essentially a Sargent colorimeter. Briefly, the obscuring power in square centimeters per gram is obtained by dividing the reciprocal of the concentration of the suspension in grams per cubic centimeter by the height of the column in centimeters. Multiplying the value thus obtained by the specific gravity of the suspended material gives the obscuring power in square centimeters per cubic centimeter.

The obscuring power method depends upon the property which the particles have of cutting off light rays. It is obviously impossible for particles to do this completely unless they can form a true geometric image of themselves. It is clear, therefore, that the obscuring power method cannot give quantitative results where the diameter of the particles is less than that necessary to form a true geometric image. For this reason the obscuring power method is totally inapplicable for the determination of particle size in colloidal systems. The same argument obtains in the case of the best pigments, such as very fine zinc oxide and gas black.

Visible light is composed of light waves varying in length from 4000 to 7000 Ångstrom units, or 0.4 μ to 0.7 μ. It has been found that, for any given wave length, particles less than one-fourth wave length in diameter do not appreciably affect the wave front. Therefore, particles less than 0.1 μ in diameter will not affect even the shortest light waves, and the obscuring power method would not be expected to give accurate quantitative results with particles less than 0.175 μ in diameter. To prove this definitely the following experiments were carried out:

Colloidal Gold—A solution of gold chloride was prepared containing 0.07 g. of gold per liter. To 250 cc. of this solution a 0.1 per cent tannin solution was added drop by drop, thoroughly agitating and warming to about 80° C. after each addition until 1 cc. had been added and the colloidal gold thus produced had passed through the cherry-red and into the green. No obscuring power reading could be obtained at this point, the solution being optically clear. Additional quantities of tannin were then added, with the following results:

Total Tannin Cc.	Obscuring Power Sq. Cm./Cc.
1	None
2	19,000
3	25,000
4	29,000
5	31,000
10	37,000
Added 5 drops 15 per cent $BaCl_2$	46,000
Added 2 cc. 15 per cent $BaCl_2$	31,000
Heated to boiling	22,000
After standing 2 days	22,000

The significant fact borne out by these experiments is that the obscuring power increases with the particle size until a maximum value is reached, after which it decreases with increasing particle size. After the barium chloride was added the particles became so large that they settled out on standing over night and the mixture had to be shaken up before the final readings were taken. The final value of 22,000 is not very different from that after 3 cc. of tannin have been added, but the particle size is many times greater.

Applications to Gas Black

The dispersions of this material obtained by previous methods[2,3] are not complete, as shown by microscopic examination and the fact that they settle out readily on standing. In an effort to improve upon the degree of dispersion various protective colloids were employed, and tannin was found to give very satisfactory results. The method developed is as follows:

Mix 50 mg. of the material into a few drops of glycerol in an agate mortar. After the pigment is thoroughly wet add 0.1 g. of solid tannin and continue trituration for 5 min. Use solid tannin instead of a solution, because it is essential to keep the original trituration mixture as concentrated in pigment as is possible for complete dispersion. Then add water, 2 cc. at a time with titration after each addition, until 10 cc. have been added. Transfer the mixture to a 250-cc. volumetric flask, add about 100 cc. water and shake thoroughly, after which fill the flask to the mark and shake again. Should the mixture foam badly it can be settled by adding a few drops of ether. Transfer 25 cc. of this dispersion to a 100-cc. volumetric flask and fill to the mark with water. After thoroughly shaking this mixture obtain the obscuring power reading in the usual way.

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[1] Presented before the Division of Rubber Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] This Journal, **12** (1920), 890.

[3] *India Rubber World*, **65** (1922), 347.

Microscopic and ultramicroscopic examination and the extremely slow rate of settling show dispersions obtained in this way to be quite complete.

Four samples of gas black were run by this method. According to ultramicroscopic examination the particle size of these increased in the order named. The following are the results of the obscuring power method:

Sample	Obscuring Power Sq. Cm./Cc.
1	9200
2	1600
3	5000
4	10,000

There is every reason to believe that Sample 2 is graphitic, which may account in part for the low obscuring power value, for reasons to be given later. However, the results plainly show that the method is of no value when applied to gas blacks, which usually contain a considerable proportion of particles less than 0.10 μ in size. As previously stated, particles less than one-fourth wave length (0.10 μ) in size will not appreciably affect even the shortest light waves. The reason for the inconsistent results on gas black is therefore perfectly obvious.

The foregoing method gives satisfactory results, however, when applied to coarser carbon pigments, such as lampblack and graphite.

APPLICATIONS TO ZINC OXIDE

To improve upon the previous methods by obtaining a better dispersion of this material, protective colloids were again tried and gum arabic was found to give the best results, both from the standpoint of dispersion and manipulative difficulties due to foaming on dilution and mixing. The following method was adopted:

Mix 0.5 g. of the material thoroughly with a few drops of glycerol in an agate mortar. To this add 10 cc. of a 1 per cent solution of gum arabic in water and continue trituration for about 5 min. Transfer the mixture to a 250-cc. volumetric flask and treat as in the case of gas black.

Three samples of zinc oxide were examined by this method. Microscopic examination and particle-size measurements, as well as obscuring power values would place them in the following order as to particle size:

Sample	Obscuring Power Sq. Cm./Cc.
1	4000
2	6000
3	6750

Particle-size measurements by the method of Green[4] have shown the particles of Sample 1 to average about 0.4 μ in diameter, while those of Sample 3 average about 0.2 μ. Sample 3 contains a considerable proportion of particles which are less than 0.1 μ and this accounts for the low obscuring power value, which should be twice that of Sample 1, or 8000.

Zinc oxides are usually much coarser than Sample 3, this being a specially prepared product. The obscuring power method is therefore generally applicable to the usual grades of this material.

APPLICATIONS TO OTHER PIGMENTS

BARYTES—A barium sulfate gel was prepared by the interaction of saturated solutions of barium iodide and manganous sulfate. Agitating this gel caused it to crystallize into a very finely divided barium sulfate. Obscuring power determinations were made on this material by the gum arabic method, as described above, and also on samples prepared by other precipitation methods and regular ground barytes. These are listed below, with their corresponding obscuring powers, in the order of increasing particle size as determined by microscopic examination and settling tests.

MATERIAL	Obscuring Power Sq. Cm./Cc.
Crystallized gel: Fresh	2260
After standing 2 mo. in paste form	3200
Precipitated: $BaCl_2$ (satd.) + H_2SO_4 (1:1)	3750
$BaCl_2$ (satd.) + H_2SO_4 (1:2)	3450
Special precipitated	2150
Regular ground	860

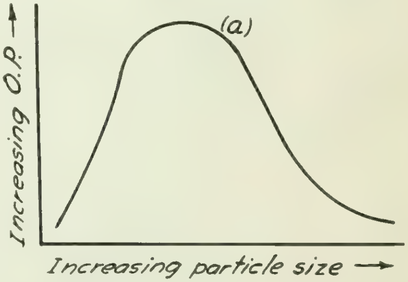
These results again point out the invalidity of the method when applied to particles which lie in the colloidal realm. The freshly crystallized gel, although many times finer than the special precipitated material, is not very different in obscuring power. Also the two-month-old sample of the crystallized gel has a higher obscuring power than the same material when freshly prepared, in spite of the fact that the crystals grew considerably during this period. The method is not even qualitative for the first two samples, but is fairly quantitative for the others.

The method has been tried out with several other pigments, and in general it can be applied with fairly quantitative results to pigments which do not contain particles smaller than 0.1 μ in diameter. It is therefore applicable to all the present-day commercial pigments with the exception of gas black and some grades of antimony pentasulfide, and iron and zinc oxides. With pigments containing particles less than 0.1 μ in size, the method is not quantitative and becomes less so as the proportion of these increases.

Owing to the great influence of the refractive index of the pigment, as well as that of the suspending medium, on the obscuring power, the values obtained for the same pigment in different media and also different pigments in the same media are not comparable. The value of the method lies in determining the relative average particle size of different samples of pigments of the same composition and crystalline structure. As previously pointed out, amorphous carbon cannot be compared with graphitic carbon because of differences in optical properties—coefficient of refraction, reflecting power.

RANGE OF APPLICABILITY

The following diagram, illustrating the range of applicability of the obscuring power method, is based on information obtained from the experiments above described.



The obscuring power-particle size curves are different for different pigments, and all show maxima in the colloidal realm. The values for obscuring power and particle size at the peak depend upon the optical properties of the substance and are different for different substances.

Obviously, the method is not applicable to pigments made up of particles which lie to the left of point (*a*) on the curve. This is the region of colloidal dispersions and in it the obscuring power increases with increase in particle size. Gas black contains a considerable proportion of particles which lie in this region. Most of the other pigments, however, are made up of particles which for the most part lie to the right of point (*a*), and to them the method can be applied with fairly accurate results.

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[4] *J. Franklin Inst.*, **192** (1921), 637.

Starch in Sorghum Juice[1]

By Sidney F. Sherwood

Office of Sugar-Plant Investigations, Bureau of Plant Industry, Department of Agriculture, Washington, D. C.

Starch, sucrose, and reducing sugars contents of the expressed juice of fifteen varieties of sorghum at time of maturity are given. The probable effect of starch upon filtration of juice, consistency of sirup, and crystallization of sucrose is briefly mentioned.

ONLY four or five out of the hundreds of samples of juice from sweet sorghum tested by the writer for the presence of starch, using the iodine test, have shown a negative reaction. In juice that has been preserved by the addition of mercuric chloride, the suspended solids separate into a more or less compact layer of greenish gray material, showing in most cases a well-defined layer or band of white starch granules. The literature contains an occasional brief reference to the presence of starch in sorghum juice, but there seems to be no printed statement giving the quantities of starch present in the expressed juice. Wiley[2] states that he never failed to obtain a positive test with the iodine reaction, Sylvester[3] measured the size of starch grains in sorghum juice, finding them to be extremely small as compared with starch from corn and potatoes. Weber and Scovell[4] report 4.12 per cent of starch in the stalks of Orange sorghum, but do not give the quantity in the expressed juice.

Wiley[5] refers to the presence of starch grains in cross sections of the stalk. Joulie[6] proposed an alcohol clarification of the cold juice, claiming as a special advantage the elimination of starch which in hot processes of clarification is converted into "dextrins" that interfere with subsequent working of the juice. Willaman, West, Spriestersbach, and Holm[7] state that starch is always found in sorghum juice, and that "as maturity approaches, the starch increases from about 0.7 per cent to 1.8 per cent." They do not give detailed results of the estimation of starch in the juice. Wiley[8] gives "starch isomers" in the dry material of two samples of sorghum blades as 21.22 and 14.49 per cent. Many references on the composition of sweet sorghum seed show that the air-dried seed contains from 65 to 70 per cent starch.

The investigation here reported was conducted in connection with breeding experiments and varietal tests of sweet sorghums.[9]

ESTIMATION OF STARCH

All samples of juice have been expressed by a small 3-roll mill from mature stalks from which the blades and seed heads had been removed. Two hundred cubic centimeters of the thoroughly mixed juice were placed in a bottle, preserved by the addition of a trace of mercuric chloride, and stored in an icebox. Other work necessitated a delay of several months before the determination could be made, and during this period the supernatant juice became perfectly clear and the sediment formed a compact layer containing a clearly differentiated starch layer or band. The clear portion was siphoned off and discarded; the entire residue was washed into a collodian dialyzing sack; a few drops of toluene were added, and the material was dialyzed against running tap water until all sugars had been removed, as indicated by negative tests with α-naphthol and with Seliwanoff's test. Ordinarily they were free in 4 days (96 hrs.). As a matter of precaution, they were then dialyzed against distilled water for 2 days (48 hrs.), changing the water several times each day. All the material in the sack was then transferred to a beaker and the starch was determined by the diastase method,[10] omitting the preliminary extraction with ether and alcohol.

The dialyzing sacks were made as follows: 9.5 g. dry pyroxylin (snowy) were dissolved in 75 cc. of ethyl ether; 60 cc. of absolute alcohol were added, and the mixture was shaken and permitted to stand until free from air bubbles. The interior of a test tube, 10 x 1.5 in., was made thoroughly wet with the solution, inverted, and permitted to drain for 2 min. The membrane was air-dried until it could be handled (approximately 0.5 hr.), and removed by flowing water between it and the wall of the tube. It was carefully examined in order to insure absence of leaks, air bubbles, etc. Membranes that were not used at once were kept immersed in water.

TABLE I—STARCH IN SORGHUM JUICE

Sample	Variety of Sorghum	Brix (17½° C.)	Corresponding Specific Gravity	Starch Per cent	Weight of Starch per Gallon G.	Weight of Starch per 100 Gallons Lbs.	Sucrose (Clerget) Per cent	Reducing Sugars (As Invert Sugar) Per cent	Ratio $\left(\frac{\%\text{ Starch plus }\%\text{ Reducing Sugar}}{\%\text{ Sucrose}}\right)$
1	Folger	20.85	1.08711	0.528	21.73	4.8	15.54	1.41	0.12
2	Japanese Ribbon	16.35	1.06718	0.178	7.19	1.6	8.45	5.99	0.73
3	Indiana Amber	20.45	1.08531	0.433	17.77	3.9	14.24	3.20	0.26
4	Farmer Jones	17.70	1.07309	0.289	11.73	2.6	11.91	2.75	0.26
5	Colman	17.55	1.07243	0.368	14.95	3.3	11.95	1.89	0.19
6	Sugar Drip	18.50	1.07662	0.443	18.06	4.0	11.77	3.05	0.30
7	Silver Top	16.20	1.06653	0.257	10.36	2.3	9.91	3.48	0.38
8	Rex X	21.50	1.09004	0.852	35.16	7.8	15.75	0.60	0.09
9	Orange	16.35	1.06718	0.275	11.12	2.5	10.56	2.38	0.25
10	Collier	20.55	1.08576	0.640	26.30	5.8	14.94	1.04	0.11
11	Texas Seeded Ribbon	16.95	1.06980	0.374	15.12	3.3	10.83	3.05	0.32
12	Planter	15.00	1.06133	0.263	10.55	2.3	9.65	1.57	0.19
13	McLean	15.35	1.06284	0.143	5.75	1.3	7.42	3.36	0.47
14	Early Folger, D. A.	15.80	1.06479	0.312	12.56	2.8	10.14	1.80	0.21
15	Honey	13.85	1.05639	0.142	5.70	1.3	6.86	4.12	0.62
			Average	0.366	14.94	3.3			
			Maximum	0.852	35.16	7.9			
			Minimum	0.142	5.70	1.3			

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[1] Received March 3, 1923.

[2] *U. S. Dept. Agr., Div. Chem., Bull.* **18** (1888), 116.

[3] *Ibid.*, **34** (1892), 77.

[4] "Report on the Manufacture of Sugar, Sirup, and Glucose from Sorghum," Illinois Industrial University, **1881**, p. 11.

[5] *U. S. Dept. Agr., Div. Chem., Bull.* **2** (1884), 6.

[6] "Etudes et experiences sur le sorgho et sucre," Paris, **1864**.

[7] *J. Agr. Research*, **18** (1919), 16, 25.

[8] *U. S. Dept. Agr., Div. Chem., Bull.* **3** (1884), 115.

[9] Project in charge of H. B. Cowgill, agronomist, under direction of C. O. Townsend, pathologist in charge, Office of Sugar-Plant Investigations, Bureau of Plant Industry.

[10] Assoc. Official Agr. Chem., Methods, **1920**, p. 95.

The sugars had been determined previously on duplicate samples of the fresh juice. The results for starch and sugars are given in Table I.

DISCUSSION

The starch content shows a comparatively wide range. Referring for convenience to the column for weight of starch in pounds per 100 gal. of juice, it will be noted that the quantity varies from 1.3 to 7.8. Separating the series arbitrarily into three groups as the starch varies 1.3 to 2.2, 2.3 to 3.2, and 3.3 to 7.8, and averaging the sucrose and reducing sugars of the samples that fall within these groups give the results in Table II.

TABLE II

Group	1.3–2.2	2.3–3.2	3.3–7.8
Number of samples in group	3	5	7
Average sucrose	7.58	10.43	13.58
Average reducing sugars	4.49	2.40	2.03

These figures indicate that a high starch content is accompanied by a high sucrose content and a low reducing sugar content, and vice versa. This is also shown very plainly by the results for Samples 8 and 15 in Table I. Either starch or reducing sugar is always present in considerable quantity, and the low ratios

$$\left(\frac{\text{Per cent starch plus per cent reducing sugar}}{\text{Per cent sucrose}}\right)$$

are usually found in samples with a high sucrose content.

Willaman, *et al.*,[11] show that as the sorghum approaches maturity there is a rapid increase in the sucrose content and a rapid decrease in the levulose and dextrose content, the dextrose decreasing at a more rapid rate than the levulose. They consider that the decrease in dextrose is due to at least three causes: (*a*) respiration; (*b*) conversion into sucrose; and (*c*) conversion to a slight extent into starch. In view of the fact that no analyses were made on immature samples, no information is available as to whether or not the metabolism of the plants conformed with Willaman's observations. In each case the juice had been obtained from plants which from appearance, hardness of seed, etc., were mature and at the stage of growth ordinarily considered suitable for the manufacture of sirup. It seems probable that the starch-sucrose-reducing sugar ratios may be characteristics of the variety.

Bulletins of the United States Department of Agriculture, Division of Chemistry (1884 to 1893), dealing with experimental work in connection with the attempted production of sugar from sorghum, show that "gummy" and "mucilaginous" constituents of the juice were responsible for extreme difficulty in clarification and filtration and that these constituents plus reducing sugars were responsible for unsatisfactory crystallization of sucrose. The gummy constituents were investigated but apparently no investigation was made on the quantities of starch present. The repeated failure of numerous attempts forty years ago to produce sugar commercially from sorghum showed quite conclusively that the commonly grown varieties of sorghum are not adapted to the production of sugar and that it is not practical to attempt to produce sugar from them. The presence in the juice of the quantities of starch and reducing sugars here shown is further evidence of this.

In view of the large areas in the United States that seem to be suited to the production of sugar beets and sugar cane, there appears to be no necessity at present to consider sorghum for sugar production. It is of great value, however, for the production of sirup, as much as 49,505,000 gal. having been produced in 1920. For this purpose, the presence of reducing sugars is desirable because it retards and, when present in sufficient amount, prevents crystallization of sucrose. In some cases the sirup-manufacturing process involves clarification of the juice with lime, followed by settling and decantation or by filtration, but probably 85 per cent of the sirup produced is made by direct open-pan evaporation of the raw juice, with removal of scums by skimming. That portion of the starch that finds its way into the finished sirup probably has a tendency to retard crystallization. However, there are indications that starch is responsible for the well-known "jellying" of sorghum sirup, and that juice low in starch will produce sirup which is more satisfactory from the standpoint of consistency and general appearance. Indications also point to starch as the cause of the great difficulty in filtering sorghum juice, especially after it has been heated.

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[11] *Loc. cit.*, p. 25.

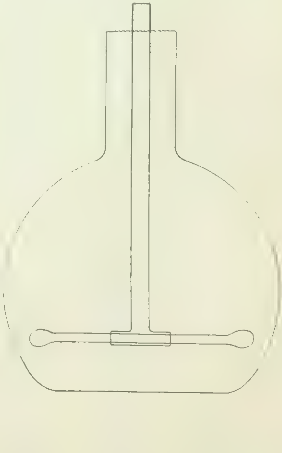
A Stirring Device[1]

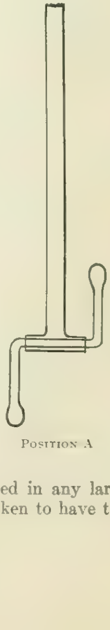
By Henry W. George

HARVARD MEDICAL SCHOOL, BOSTON, MASS

In carrying out a reaction in a narrow-neck, balloon-shaped flask it is difficult to introduce a stirrer with arms long enough to extend close to the walls of the flask. To overcome this difficulty the following piece of apparatus has been developed:

A glass T-tube with short arms is sealed to a long glass rod, and another rod of slightly smaller diameter than the tubing is passed through the T. The rod is bent at right angles close to the arms of the T so that the ends of the rod point in opposite directions. The rod is then flattened at each end. To insert into the flask the movable glass rod is fixed so that the arms are vertical (Position A). After the stirrer has passed through the neck of the flask, it is jarred sharply and the movable rod falls so that the arms assume a horizontal position. When the stirrer rotates the paddles remain horizontal and cause vigorous agitation throughout the contents of the flask.





POSITION A

Evidently, such an apparatus can be used in any large flask with a small neck. Care should be taken to have the movable rod evenly balanced.

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[1] Received April 12, 1923.

Propionic Acid and Ketones from Whey[1]

By **E. O. Whittier** and **J. M. Sherman**

Research Laboratories, Dairy Division, Department of Agriculture, Washington, D. C.

The factors affecting the propionic fermentation of lactose have been investigated, and conditions determined whereby approximately 2.4 lbs. of propionic acid and 1 lb. of acetic acid may be obtained from 5 lbs. of lactose in 12 days' incubation.

A mixed culture of Bacterium acidi propionici (d) and Lactobacillus casei, incubated at 30° C. for 3 days, is used for the inoculation of the previously sterilized and buffered whey.

The mixture of propionate and acetate obtained may be either converted into free acids and refined, or distilled to yield a mixture of acetone, methylethyl ketone, and diethyl ketone.

LACTOSE is a substance of such slight utility at present that tremendous amounts are run to waste as whey. The demand for refined lactose for use in infant feeding is satisfied by an insignificant proportion of the amount that could be produced. The manager of a western creamery recently stated that his company alone would like a market for 5,000,000 lbs. of lactose annually. The cost of production of milk albumin, for which a demand is developing, is bound up with the problem of disposal of the crude lactose produced from the whey along with the albumin.

The results reported in this article are the outcome of one of several investigations undertaken in the laboratories of the Dairy Division in an effort to devise a method for the commercial utilization of lactose.

PROPIONIC ACID

The amount of propionic acid produced and marketed at the present time is very small. The chief and probably sole commercial source of this acid is the residue from the refining of acetic acid. Perfume manufacturers use practically all that is consumed, converting it into various esters. The use of ethyl propionate as a pyroxylin solvent has been patented,[2] and propionyl cellulose has been suggested as a possible substitute for acetyl cellulose.[3] The wide temperature range in which propionic acid is fluid (−22° to + 140° C.) indicates that it might advantageously replace acetic acid as a solvent under some conditions. Development of a cheap source of propionic acid should considerably stimulate its use.

Previous work is summarized and a number of experiments are reported by Sherman and Shaw in an article appearing elsewhere.

EXPERIMENTAL—The propionic organism used in this work was *Bacterium acidi propionici* (*d*), isolated by Sherman in his work on Swiss cheese,[4] and commonly referred to in this laboratory as Culture *62*. One hundred cubic centimeters of medium were used for each experiment, inoculated with 1 cc. of a *62* culture unless otherwise specified, and incubated at 30° C. At the end of the incubation period the material was transferred to a 100-cc. graduated flask, made up to the mark, transferred to a centrifuge tube without rinsing, and whirled for 5 min. A 50 or 75-cc. aliquot of the clear liquid was pipetted into a 500-cc. round-bottomed flask, made acid to Congo red with 10 per cent sulfuric acid, diluted to a volume of about 250 cc., and steam-distilled at approximately constant volume till 1000 cc. of distillate had been collected. An aliquot of the distillate was titrated with 0.05 *N* sodium hydroxide to determine total volatile acid present. A volume requiring approximately 28 cc. 0.05 *N* sodium hydroxide was made alkaline to phenolphthalein and evaporated to about 60 cc. It was then transferred to a 110-cc. graduated flask, made acid to Congo red with 10 per cent sulfuric acid, diluted to the mark, and transferred to a 200-cc. flask without rinsing. It was then slowly distilled, five 20-cc. portions of distillate being collected and titrated with 0.05 *N* sodium hydroxide. The ratio of propionic to acetic acid and the actual weight of each acid present were calculated from these data and Duclaux tables. The Duclaux method gave very consistent results; it is difficult to understand why investigators so frequently attempt to modify it.

One of the chief objections to almost any fermentation is the excessive time factor. Preliminary experiments showed that a 5 per cent lactose solution containing peptone and the propionic organism was only about 10 per cent converted to volatile acid in 14 days. Aerobic fermentations may be greatly accelerated by aeration methods, but such a scheme is of no benefit in an anaerobic process.

DETERMINATION OF MOST DESIRABLE pH VALUE—Most bacteria are quite sensitive to changes in hydrogen-ion concentration. To determine the most desirable pH value for the propionic organism, the series recorded in Table I was carried out. Organism *8* is *Lactobacillus casei*, an accelerator of the growth of the propionic organism, *62*. Each culture contained 2 g. calcium lactate and 1 g. peptone, and was incubated for 14 days. It will be noted that the amount of acceleration caused by *Lactobacillus casei* is very small in this series, especially in comparison with the acceleration indicated in the following tables. This is probably due to the fact that *Lactobacillus casei* does not grow well in the medium used.

TABLE I—EFFECT OF DIFFERENT H-ION CONCENTRATIONS ON RATE OF PROPIONIC FERMENTATION

No	Inoculating Organisms	pH Initial	Ratio of Mols. Propionic to Mols. Acetic	Weight of Acid Produced Propionic G.	Weight of Acid Produced Acetic G.
1	*62*	5		About 0.05 g. volatile acid	
2	*62*	6	2.01	0.5599	0.2137
3	*62*	7	2.05	0.6526	0.2582
4	*62*	8	2.33	0.5895	0.2048
5	*62,8*	5		About 0.04 g. volatile acid	
6	*62,8*	6	2.11	0.6028	0.2323
7	*62,8*	7	2.04	0.6621	0.2635
8	*62,8*	8	2.40	0.6324	0.2137

Growth of the propionic organism is practically nil at the H-ion concentration represented by pH 5. The so-called neutral point, pH 7, is the most desirable reaction for the growth of the organism, a change in pH in either direction retarding the production of acid. In subsequent experiments, 5 g. of calcium carbonate were added to each 100 cc. culture to maintain the pH value at approximately 7, and the cultures were gently shaken every few days.

EFFECT OF ORGANISMS ON ACID RATIO—In most of our experiments, a fairly constant ratio of 2 molecules of propionic acid to 1 molecule of acetic acid was obtained, but frequently the ratio was noticeably disturbed. In several cases this was attributed to contaminating organisms or to accelerating organisms purposely introduced. To get at the mechanism of this effect, cultures were made containing, instead of lactose, sodium propionate and acetate, and these were inoculated with organisms of several types. Culture *45.4* is an unidentified organism known to accelerate the propionic fermentation. The results after 19 days' incubation are shown in Table II.[5]

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] U. S. Patents 1,397,173 and 1,397,493 (1921).

[3] Dubosc, *Rev. prod. chim.*, **24** (1921), 499.

[4] *J. Bact.*, **6** (1921), 379

TABLE II EFFECT OF VARIOUS ORGANISMS ON PROPIONIC AND ACETIC ACIDS

No.	Inoculating Organism	Ratio of Mols. Propionic to Mols. Acetic	Weight of Acid Found		Acid Destroyed	
			Propionic G.	Acetic G.	Propionic %	Acetic %
Sterile, average of three		1.67	0.6637	0.3072	..	..
9	*Bacillus subtilis*	2.09	0.6709	0.2606	0	15.2
10	*Proteus*	2.57	0.6596	0.2075	0	32.6
11	*Proteus vulgaris*	3.50	0.6603	0.1528	0	50.4
12	*45.4*	5.67	0.3399	0.0488	46.4	84.4

Sherman and Shaw report *Lactobacillus casei* as a more effective accelerator than *45.5*. This may be due only to the destructive activity on both volatile acids produced. The results reported above show further that organisms of the *Proteus* type may be used to purify propionic acid from acetic acid, though the time factor is considerable.

With the idea of nullifying this time factor as much as possible, an attempt was made to carry on the fermentation and purification simultaneously. The results are shown in Table III. Controls are included for comparison. Culture *62* is the propionic organism; *8* is *Lactobacillus casei*, used for accelèrative purposes; *11o* is *Proteus vulgaris*. The media contained 5 g. lactose, 5 g. calcium carbonate, and 1 g. yeast.

TABLE III EFFECT OF PRESENCE OF *Proteus Vulgaris* ON PROPIONIC FERMENTATION

No.	Inoculating Organisms	Incubating Period Days	Ratio of Mols. Propionic to Mols. Acetic	Weight of Acid Produced		Per cent of Theoretical Yield	
				Propionic G.	Acetic G.	Propionic	Acetic
13	*11o*	30	Formic and butyric acids only				
14	*62*	30	1.41	0.4971	0.2859	18.1	25.8
15	*62,11o*	30	1.50	1.3442	0.7266	49.1	65.5
16	*62,8*	30	2.47	2.3517	0.7713	85.8	69.5
17	*62,8,11o*	33	2.09	2.3231	0.8988	84.8	80.8
18	*62*	44	1.40	0.5799	0.3380	21.2	30.5
19	*62,11o*	44	1.56	1.4741	0.7643	53.8	68.9
20	*62,8*	44	2.72	2.4387	0.7209	89.0	64.9
21	*62,8,11o*	44	2.12	2.3636	0.9020	86.3	81.3

It will be seen that when used in combination with other organisms, *Proteus vulgaris* does not selectively destroy acetic acid. In fact, when used with both the propionic organism and *Lactobacillus casei*, it appears to inhibit the destruction of acetic acid. Evidently, the effect an organism will have in mixed culture cannot safely be predicted from its conduct in pure culture. If *Proteus* is to be used for elimination of acetic acid, it must be used by itself. Incidentally, it may be noted that *Proteus vulgaris* of itself exerts an accelerative action on the propionic fermentation.

COMPARISON OF VARIOUS SOURCES OF NITROGEN—To compare the efficiency of *45.4* and *Lactobacillus casei* as accelerators, and to determine the relative utility of various sources of nitrogen, a series of experiments was run, part of the results from which are given in Table IV. A per cent of theory yield is calculated for the whey cultures, based on the assumption that 100 cc. of whey contains 5 g. of lactose. This is justifiable for purposes of comparison, and is very close to fact. The incubation period in the experiments reported was 42 days.

TABLE IV RELATIVE UTILITY OF VARIOUS SOURCES OF NITROGEN

No.	Lactose G.	Nitrogen Source (1 G.)	Inoculating Organisms	Ratio of Mols. Propionic to Mols. Acetic	Weight of Acid Produced		Per cent of Theoretical Yield	
					Propionic G.	Acetic G.	Propionic	Acetic
22	5	Peptone	*62*	3.17	1.3538	0.3466	49.4	31.2
23	5	Yeast	*62*	1.84	0.7081	0.3118	25.8	28.1
24	Whey	Whey	*62*	2.12	0.4891	0.1865	17.8[a]	16.8[a]
25	5	Peptone	*62,45.4*	3.17	0.7763	0.1989	28.3	17.9
26	5	Yeast	*62,45.4*	1.70	0.9497	0.4522	34.7	40.7
27	Whey	Whey	*62,45.4*	2.25	1.7612	0.6328	64.3[a]	57.0[a]
28	5	Peptone	*62,8*	2.08	1.7705	0.6913	64.6	62.3
29	5	Yeast	*62,8*	2.16	2.2041	0.8260	80.4	74.4
30	Whey	Whey	*62,8*	1.95	2.4039	0.9998	87.8[a]	90.1[a]

[a] Per cent of theory yield calculated for the whey cultures on the assumption that 100 cc. of whey contains 5 g. of lactose.

The table shows clearly that the proteins of whey are more stimulating to the mixed cultures than either peptone or yeast. Since mixed cultures show considerable advantage over pure cultures for practical use, it is fortunate that fortification of the nitrogen source in whey is not necessary.

The choice of nitrogen source appears consistently to influence the ratio of propionic to acetic acid, but since this should come about only through its influence on the destruction of the volatile acids first produced, and since all volatile acid decomposed appears to be acetic, the effect may be disregarded for practical purposes. The difference in the destructive activity of *45.4* on volatile acids by itself and in mixed culture may be seen by a comparison of data in Tables II and IV.

Table IV shows conclusively that an accelerating organism is highly desirable, that *Lactobacillus casei* is a more effective accelerator than *45.4* and that whey is better than an artificial medium for the activities of the propionic organism plus *Lactobacillus casei*.

EFFECT OF LACTOSE—Sherman and Shaw have shown that about 95 per cent of the lactose fermented can be accounted for on the basis of the Fitz reaction[6] as propionic and acetic acids. In Tables III and IV, several runs occur in which yields of about 85 per cent have been obtained, the calculation being based on the total quantity of lactose present. Under these conditions, then, about 90 per cent of the lactose present was fermented, which is as much as may reasonably be expected. To obtain this yield at least a month's incubation has been necessary. While this period is excessive for practical production from crude whey, it might not be impractical if a whey containing a high percentage of lactose could be used. To test this possibility, the series shown in Table V was run. Cultures were made up with crude whey, and with the same whey to which 5 per cent and 10 per cent lactose had been added.

TABLE V EFFECT OF ADDED LACTOSE ON PROPIONIC FERMENTATION OF WHEY

No.	Whey Cc.	Lactose G.	Inoculating Organisms	Incubating Period Days	Ratio of Mols. Propionic to Mols. Acetic	Weight of Acid Produced	
						Propionic G.	Acetic G.
31	100	0	*62,8*	9	2.00	1.4595	0.5878
32	100	5	*62,8*	9	2.33	1.4013	0.4870
33	100	10	*62,8*	9	2.35	0.9863	0.3396
34	100	0	*62,8*	14	2.18	2.3118	0.8621
35	100	5	*62,8*	14	2.12	1.6113	0.6066
36	100	10	*62,8*	14	1.97	1.2893	0.5315

The results show that, not only was the additional quantity of lactose not converted to volatile acids, but the increased concentration of lactose actually retarded the fermentation.

EFFECT OF CONDITIONS IN CULTURES—In order to test the effect of conditions in the inoculating cultures upon the fermentation, both pure and mixed cultures of the propionic organism and *Lactobacillus casei* were grown for different periods before being used for inoculation of test cultures of whey. The results are given in Table VI.

TABLE VI EFFECT OF HABITUATION OF PROPIONIC AND ACCELERATIVE ORGANISMS TO EACH OTHER

No.	Inoculating Organisms	How Grown	Age Days	Incubating Period Days	Ratio of Mols. Propionic to Mols. Acetic	Weight of Acid Produced	
						Propionic G.	Acetic G.
37	1% *62*,1% *8*	Apart	3	7	1.82	0.6573	0.2919
38	1% *62*,1% *8*	Apart	3	7	2.08	0.6560	0.2563
39	1% *62,8*	Together	3	7	2.78	1.5063	0.4428
40	1% *62,8*	Together	3	7	2.25	1.2760	0.4584
41	1% *62*,1% *8*	Apart	13	7	2.23	1.0527	0.3816
42	1% *62*,1% *8*	Apart	13	7	2.12	1.1232	0.4288
43	1% *62,8*	Together	13	7	2.13	1.3711	0.5219
44	1% *62,8*	Together	13	7	2.33	1.3083	0.4546

It appears to be advantageous to grow the inoculating organisms together, especially if they are to be used within 2 or 3 days. The difference in the potential activities of the

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[5] U. S. Patent 1,450,392 (1923).

[6] *Ber.*, **11** (1878), 1890; **12** (1879), 474; **13** (1880), 1306.

TABLE VII—EFFECT OF AMOUNT OF INOCULATION ON PROPIONIC FERMENTATION

No.	Whey Cc.	Inoculation Cc.	Incubating Period Days	Ratio of Mols Propionic to Mols Acetic	Weight of Acid Produced Propionic G.	Weight of Acid Produced Acetic G.	Weight of Acid Produced Calculated to 100 Cc. Propionic G.	Weight of Acid Produced Calculated to 100 Cc. Acetic G.	Per cent of Theoretical Yield[a] Propionic	Per cent of Theoretical Yield[a] Acetic
45	100	1	3		Contaminated butyric acid present					
46	95	5	3	2.23	0.8417	0.3053	0.8869	0.3213	32.2	29.0
47	90	10	3	2.22	0.8397	0.3059	0.9330	0.3400	34.1	30.6
48	80	20	3	2.50	0.9055	0.2943	1.1319	0.3679	41.3	33.2
49	100	1	6	2.01	0.8414	0.3990	0.8414	0.3990	30.7	30.6
50	95	5	6	2.46	1.3226	0.4366	1.3922	0.4595	50.8	41.4
51	90	10	6	2.53	1.3135	0.4204	1.4593	0.4671	53.3	42.1
52	80	20	6	2.36	1.3099	0.4487	1.6374	0.5609	59.7	50.5
53	100	1	9	1.90	1.2980	0.5546	1.2980	0.5546	47.4	50.0
54	95	5	9	2.15	1.6183	0.6041	1.7035	0.6359	62.1	57.3
55	90	10	9	2.26	1.7403	0.6223	1.9336	0.6914	70.6	62.3
56	80	20	9	2.60	1.8831	0.5881	2.3539	0.7351	85.9	66.2

[a] These values are calculated for the whey cultures on the assumption that 100 cc. of whey contain 5 g. of lactose.

cultures disappears largely after about 2 wks., the separately grown cultures becoming nearly as effective as those grown together.

EFFECT OF VARYING AMOUNTS OF INOCULUM—With an organism growing so slowly as the propionic bacterium, the amount of inoculating medium should have considerable influence on the rate of fermentation, particularly in the first 10 days. Therefore, a series was run using various amounts of inoculum, other conditions being the most favorable which had been discovered in previous series. A mixed culture of the propionic organism and *Lactobacillus casei* was grown in whey for 11 days and then used for inoculation. The volatile acid in the inoculating culture at the time of its use was determined, and corrections were applied to the results obtained. The values in each experiment were calculated to the basis of 100 cc. of whey for comparison. No correction could be determined which would account for the acids produced after inoculation from the lactose still present in the inoculating culture. However, since the quantities of unfermented lactose present in the amounts of inoculum used must have been rather small, the comparison of results from samples incubated the same length of time cannot be appreciably affected. The results are shown in Table VII.

It is clear that 1 per cent inoculation is by no means sufficient to obtain the most rapid rate of fermentation. Increasing the amount of inoculation above 5 per cent shows only slight advantage. Five per cent is undoubtedly the most practical quantity to use.

While there are probably other effective means of accelerating the propionic fermentation, they are mostly factors that cannot be handled satisfactorily in the laboratory, but are bound up with the design and operation of large-scale equipment. Eventually, our minimum time of 12 days' incubation for an 85 per cent yield could probably be considerably diminished. With the development of a demand for propionic acid, it should be possible to meet it at a reasonable cost by this process.

KETONES

There is a growing demand for solvents with the general properties of acetone, but with higher boiling points and lower solubility in water. For a long time acetone has been made on a large scale by the distillation of calcium acetate and of wood. Within recent years patents have been obtained for the catalytic conversion of acetic acid vapors into acetone.[7]

These methods, applied to calcium propionate and propionic acid, respectively, yield diethyl ketone, b. p. 102.7° C., slightly soluble in water. If a mixture of acetate and propionate, or of the acids, is used, the product contains acetone, methylethyl ketone, and diethyl ketone.[8] Methylethyl ketone boils at 81° C., and has a solubility in water intermediate between acetone and diethyl ketone. A mixture of ketones, evidently containing chiefly methylethyl ketone, is obtained from the distillation of the calcium salts extracted from wool scourings.[9] This mixture has been recommended as a denaturant for ethyl alcohol.

On the assumption that the volatile acids from the propionic fermentation exist in the proportion of 2 molecules of propionic to 1 of acetic—which they closely approximate—the limiting theoretical possibilities in the ratios of the constituents of the acetone oil obtained therefrom are 37.4 per cent diethyl ketone, 62.6 per cent methylethyl ketone, and no acetone, on the one hand, and 74.8 per cent diethyl ketone, no methylethyl ketone, and 25.2 per cent acetone, on the other. Some combination of values between these limits is to be expected.

With the idea of determining roughly the possibilities of the ketone conversion as a means of utilizing the product of the propionic fermentation, several distillations of dried calcium salts were carried out. The products in each case gave nearly identical distillation curves. Several attempts to determine the proportion of the components by chemical means failed to give satisfactory differentiation of the ketones. Finally, repeated fractionation through a narrow 2-ft. column of beads was resorted to. The final distribution of the fractions indicated approximately 20 per cent acetone, 40 per cent methylethyl ketone, and 40 per cent diethyl ketone.

Because of incomplete conversion of the calcium salts due to lack of agitation in the retorts, and because of frequent cracking of the retorts, no reliable yield data were obtained. With continuous operation, there is no doubt that as satisfactory yields can be secured as are obtained in calcium acetate distillation.

It is advisable to distil off the volatile acids from the fermentation mixture and to reconvert to calcium salts before the dry distillation. Distillation of the evaporated fermentation mixture without previous purification gives considerable quantities of evil smelling protein decomposition products that are difficult to eliminate satisfactorily in the subsequent fractionation.

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[7] Brit. Patent 14,085 (1915); U. S. Patent 1,315,544 (1919); U. S. Patent, 1,315,525 (1919).

[8] Schramm, *Ber.*, **16** (1883), 1581.

[9] A. and P. Buisine, *Comp. rend.*, **128** (1889), 561.

Frank Cummings Cook

Frank Cummings Cook, M.A., M.S., Yale; Ph.D., George Washington, died in Dallas, Texas, on June 19, after an operation for appendicitis.

Since leaving Yale in 1904, Dr. Cook had been connected with the Bureau of Chemistry, U. S. Department of Agriculture. At the time of his death, he was engaged in special research work on the control of insects infesting live stock, and was temporarily located at Dallas, Texas. He was a member of the American Chemical Society, the Association of Official Agricultural Chemists, the Society of Biological Chemists, the Washington Academy of Sciences, and was a delegate to the International Congress of Applied Chemistry at Rome, 1906, and at London, 1909. He was the author of numerous papers and bulletins on food metabolism, enzymes, insecticides, fungicides, and related subjects.

Dr. Cook had a host of friends in the chemical fraternity, by whom his untimely death will be keenly felt. He is survived by a wife and one son.

Methyl Anthranilate in Grape Beverages and Flavors[1]

By R. D. Scott

Ohio State Department of Health, Columbus, Ohio

IN THE EXAMINATION soft drinks and concentrated fruit flavors the determination of methyl anthranilate, $C_6H_4.NH_2.COOCH_3$, is of unusual value. While found chiefly in grape-type products, this ester is unique in being susceptible of exact determination, even when present in high dilution. Its natural occurrence is described by Gildemeister,[2] who states that "it was discovered in 1895 by Walbaum in neroli oil and has since been found in the oils of tuberose, **** ylang-ylang, Spanish orange blossoms, sweet orange rind, **** bergamot leaves, jasmin flowers and gardenia." He also infers its presence, by the odor, in certain species of apples.

Soft-drink flavors are frequently submitted to food control officials to secure a decision on the conformity of their labels to law, which means essentially whether they are true fruit or imitation products. In such cases it is feasible to ascertain the nature of the grape flavor in the lot submitted by determining its methyl anthranilate content, while it may be impossible to decide with certainty that the other fruit flavors are or are not true products.

Literature on the estimation of the ester is not extensive. Power[3] reviews the previous work on the subject and outlines a colorimetric method based on the work of Erdmann,[4] whose method seems best adapted, in principle, for its estimation in the products mentioned above. Briefly, Erdmann's method is as follows: The diazotized solution of methyl anthranilate is run from a buret into a standard alkaline solution of β-naphthol. From time to time the precipitated red dye is filtered off and a portion of the filtrate is tested with more of the diazotized ester solution until no further precipitation occurs. The reactions involved may be expressed:

$$C_6H_4.NH_2.COOCH_3 + NaNO_2 + 2HCl = C_6H_4.N_2Cl.COOH_3 + NaCl + 2H_2O \quad (1)$$

$$C_6H_4.N_2Cl.COOH_3 + C_{10}H_7.OH + NaOH = C_6H_4.COOH_3.N:N.C_{10}H_6OH + NaCl + H_2O \quad (2)$$

Experimental

In the application of Erdmann's method it was found that (1) concordant results could be obtained only when the amount of alkali present was carefully adjusted to be equal to, or but slightly in excess of, that required by theory; (2) approximately 5 per cent more than the theoretical amount of diazotized methyl anthranilate was required to combine with a given amount of β-naphthol, but on substituting α-naphthol nearly the theoretical amount was required; (3) with either α- or β-naphthol excessive amounts of methyl anthranilate were required if the time of diazotization was long continued; (4) definite end-points could be obtained only with fairly strong solutions of methyl anthranilate, 0.5 g. being the minimum amount which could be titrated with accuracy; and (5) titration is tedious and time consuming.

It was thought that a gravimetric method might be more satisfactory, and a study of the various factors influencing the reactions was made.

Purification of Reagents—The methyl anthranilate used was that ordinarily supplied to extract manufacturers. It was in the form of large, colorless crystals, melting readily to a straw-colored liquid. A quantity was dissolved in ether, concentrated hydrochloric acid solution was added, and the hydrochloride which immediately precipitated was filtered off with suction and washed twice with ether. After solution in absolute methanol, the hydrochloride was reprecipitated with ether, filtered, washed with ether, and neutralized with sodium carbonate solution. The liberated ester was washed with water in a separatory funnel, drawn off, dried with ignited potassium carbonate, and filtered. This purified ester melted to a colorless liquid at 25° C. The α- and β-naphthols used were the C. P. grades, further purified by subliming in large covered beakers, over a water bath, for 3 or 4 days.

Solubility of Dye—The solubility of the dye in water was first studied. A quantity was precipitated and washed repeatedly with water to remove soluble salts. The evaporated residue from 100 cc. of the aqueous solution, saturated at 25° C., weighed 0.0011 g. The solubility in alkalies was then noted. Portions of 0.05 g. of the powdered dye were treated with 10 cc. of normal solutions of sodium hydroxide, sodium carbonate, and sodium bicarbonate. After shaking at intervals for 3 days, each solution was filtered through Gooch crucibles, washed, dried, and weighed. The loss in weight was 0.0130, 0.0036, and 0.0010 g., with sodium hydroxide, sodium carbonate, and sodium bicarbonate, respectively. These results indicate that the solubility of the dye increases as the hydroxyl-ion concentration increases and that sodium bicarbonate is the most suitable alkali to use in order that the solubility error may be low. It is pointed out by Mathewson[5] that a similar dye, diazotized methyl anthranilate coupled with α-naphtholsulfonate, is gradually saponified in sodium carbonate solution. The alkaline solution used by Erdmann and by Power was a mixture of sodium hydroxide and sodium carbonate, sodium hydroxide being used to effect solution of β-naphthol. This, however, introduces an undesirable variable concentration of the alkali in the solution precipitated. A 0.2 per cent solution of either α- or β-naphthol in 30 per cent ethyl alcohol was stable. Accordingly, this alcoholic naphthol solution was substituted.

Time of Diazotization—1.5582 g. of methyl anthranilate were dissolved in 250 cc. of ethyl alcohol. Aliquots of 5 cc. or 0.03116 g. were made up to 100 cc. with water and diazotized with 2 cc. of *N* hydrochloric acid and 1 cc. of 5 per cent sodium nitrite. At intervals the diazotized samples were poured into beakers containing 20 cc. of 0.2 per cent alcoholic β-naphthol and 3 cc. of *N* sodium bicarbonate. After standing over night, the precipitates were filtered through weighed Gooch crucibles, washed with 50 cc. of water, and dried at 100° C. for 2 hrs. Weights in grams of precipitates from solutions diazotized as noted were: 10 sec., 0.0592; 30 sec., 0.0594; 1 min., 0.0594; 10 min., 0.0588; 1 hr., 0.0560; 5 hrs., 0.0496; 20 hrs., none. Theory, 0.0631 g.

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[1] Received October 23, 1922.

[2] "The Volatile Oils," 2nd Ed., Vol. 1.

[3] *J. Am. Chem. Soc.*, **43** (1921), 377.

[4] *Ber.*, **35** (1902), 24.

[5] *J. Assoc. Official Agr. Chem.*, **6** (1922), 16.

Erdmann allowed 10 min. for diazotization, but 1 min. appears sufficient. The time should not be too long, as the diazo compound is gradually hydrolyzed to methyl salicylate.

RESULTS WITH α- AND β-NAPHTHOLS—Aliquots of 0.03116 g. from the solution of methyl anthranilate were taken, diazotized for 1 min., and poured into varying quantities of 0.2 per cent α- and β-naphthol solutions in 30 per cent ethyl alcohol, adding sodium bicarbonate solution in 50 per cent excess. Weights in grams of precipitates with volumes of β-naphthol were as follows: 15 cc., or calculated amount, 0.0580; 22.5 cc., 0.0588; 30 cc., 0.0584; 60 cc., 0.0560. The results with α-naphthol were: 15 cc., or calculated amount, 0.0610; 22.5 cc., 0.0628; 30 cc., 0.0628; 60 cc., 0.0582. Theory, 0.0631 g. While low results were obtained with β-naphthol, the results with α-naphthol were close to theory. Precipitation with α-naphthol took place very quickly, the light, bulky precipitate rising to the surface. With β-naphthol several hours are necessary for complete precipitation.

RESULTS WITH VARIOUS ALKALIES—To study in greater detail the action of different alkalies, the following series was run: Aliquots of 0.0324 g. of an alcoholic solution of methyl anthranilate were made up to 200 cc. with water, diazotized for 1 min. with 5 cc. of *N* hydrochloric acid and 2 cc. of 5 per cent of sodium nitrite solution, and poured into beakers containing 20 cc. of 0.2 per cent solution of α-naphthol in 30 per cent ethyl alcohol, plus volumes of alkali noted. The weights of the precipitates thus obtained are given in Table I.

TABLE I—WEIGHTS OF PRECIPITATES (THEORY, 0.0656 G.)

Normal Alkali Cc.	NaOH G.	Na_2CO_3 G.	$NaHCO_3$ G.
5	0.0602	0.0634	0.0652
7.5	0.0540	0.0622	0.0648
10	0.0318	0.0592	0.0624
20	0.0130	0.0480	0.0588

The results with sodium bicarbonate as alkali are near theory. A moderate excess did not greatly lower the yield of precipitate.

COLORIMETRIC METHOD—For colorimetric estimation of the ester, sodium hydroxide is the more suitable alkali, since, owing to its greater solvent action, higher concentrations of the dye remain in solution. While either of the naphthols gives a good color series, the colors produced when the alpha form is used are very much deeper. The following quantities of methyl anthranilate form a satisfactory series of standards: blank, 0.000005, 0.00001, 0.000025, 0.00005, 0.0001, 0.00015, and 0.00025 g. These quantities diazotized for 30 sec. in 100 cc. with 1 cc. of *N* hydrochloric acid and 0.5 cc. of 5 per cent sodium nitrite are poured into Nessler jars containing 0.5 cc. of 2 per cent alcoholic α-naphthol solution and 3 cc. of *N* sodium nitrite. The maximum color develops within 15 min. and remains constant for several hours. A very slight color change occurs in the blank tube, but the difference between it and the tube containing 0.000005 g. of the ester is pronounced. Amounts over 0.00025 g. produce colors rather too deep to be satisfactorily compared.

EXAMINATION OF COMMERCIAL PRODUCTS

The methods developed were applied in the examination of grape juices, grape "pops" or bottled soft drinks artificially colored and flavored, and concentrated "grape" extracts used in compounding pops. The results are shown in Table II.

GRAPE JUICES—Having determined, by collecting a series of distillates from 500-cc. samples, that practically all the ester was carried over in the first 500-cc., this volume was in each case steam-distilled, using a mercury seal and cooling the receiving flask in ice water. A 100-cc. aliquot of the distillate was treated and compared with a series of methyl anthranilate standards as described in the preceding paragraph. The samples examined were believed to be pure. Eight brands of Concord juice contained from 0.80 to 1.49 parts per million, and four brands of Catawba juice contained from 0.11 to 0.40 part per million of the ester. Power and Chestnut[6] found that methyl anthranilate contents did not exceed 2 and 0.2 part per million with Concord and light-colored juices, respectively.

TABLE II—METHYL ANTHRANILATE CONTENT OF COMMERCIAL GRAPE PRODUCTS

GRAPE JUICES				POPS		CONCENTRATED EXTRACTS	
Concord		Catawba					
Brand	P. p. m.	Brand	P. p. m.	Ser. No.	P. p. m.	Ser. No.	G. per 100 cc.
P	1.49	WS	0.40	8964	17.5	8632	0.342
RP	1.42	BS	0.13	8965	17.0	B	0.270
VK	1.46	A	0.11	8556	7.3	B-1	0.320
W	1.18	M	0.08	8915	7.1	B-2	0.513
BS	1.12					B-3	0.477
G	0.96					B-4	0.510
AP	0.80						

GRAPE POPS—One hundred cubic centimeter volumes were steam-distilled to 500 cc., and 100-cc. or 50-cc. aliquots of the distillate were taken for colorimetric estimation.

ARTIFICIAL GRAPE CONCENTRATED EXTRACTS—After preliminary study, the following method was applied: 25 cc. of sample were diluted to 100 cc. and steam-distilled to 500 cc., using a mercury seal and cooling the receiving flask in ice water. An aliquot of 200 cc. was diazotized for 1 min. with 5 cc. of *N* hydrochloric acid and 2 cc. of 5 per cent sodium nitrite solution. The diazotized solution was poured into 25 cc. of 0.2 per cent solution of α-naphthol in 30 per cent ethyl alcohol, and 6 cc. of *N* sodium bicarbonate. After 10 min. the precipitate was filtered on a 30-cc. weighed Gooch crucible, washed with 100 cc. of water, dried at 100° C. for 2 hrs., and weighed. Weight precipitate times 0.4935 equals weight of methyl anthranilate.

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[6] *J. Am. Chem. Soc.*, **43** (1921), 1741.

Meeting of Stamford Chemical Society

The Stamford Chemical Society held its May meeting on the 28th at the Suburban Club, where about fifty men attended the dinner which preceded the evening program. Of these at least 20 per cent were business men and the gathering was especially honored by the presence of Hon. Schuyler Merritt, U. S. Congressman of the district. R. H. Stevens, president of the society, presided, and described the work of the society during the year. He introduced H. W. Banks, 3rd, who had been elected the next president. Mr. Banks spoke of his special interests in the coming work of the society and introduced Charles Wadsworth, 3rd, who acted as toastmaster. Mr. Wadsworth presented the Hon. Schuyler Merritt, who spoke on the lack of appreciation of chemistry during the last few years and referred to his own brief contact with the science in college days. He paid an extended tribute to the war activity of chemists. He spoke at length of the need of science for world progress and emphasized his belief that science quickened and illuminated by religion will make possible the solution of present-day difficulties.

F. H. Getman then described the work of the educational committee, which will soon award the prize of ten dollars for the best essay on chemistry in everyday life, common chemicals in the home, or chemistry in our local industries, submitted by high-school students in Stamford. Following out the suggestion that chemists coöperate in carrying the message of chemistry to American women along the lines outlined in the Plea to American Women, the Committee on Education has been in communication with the Stamford Women's Club, and arrangements have been made to include at least one address on chemistry during the next season.

The final speaker of the evening was H. E. Howe, who spoke on "Factors in Scientific Progress," stressing the importance of organization as one of the outstanding requirements in furthering scientific work.

Automatic Fractionating Columns[1]

By **Wm. A. Peters, Jr.**

E. I. du Pont de Nemours & Co., Wilmington, Del.

THE first fractional distillations were carried out in batch stills, and the operation required careful watching at all times and repeated distillations to obtain a high degree of separation. Later, the continuous rectifier was developed for certain fractionations and, since the rectifier might be regarded as a series of small stills operating simultaneously, the labor required for a given output was considerably reduced.

If the composition of the feed and all other conditions were maintained absolutely constant, it might be possible to run a continuous rectifier indefinitely without any attention and obtain a satisfactory product. The important details of such a rectifier for separating alcohol and water are shown in Fig. 1. The divisions shown in the column represent theoretical plates.[2] A theoretical plate is defined as one on which the liquid covering it is of the same composition throughout, while all the vapor rising from it is in equilibrium with this liquid. It therefore represents a certain height of column rather than one or more actual plates of a plate column, and this same conception can be applied equally well to a packed column. In fact, all our small automatic columns are packed with glass rings, a type of construction that is much cheaper than the plate column for the smaller units. It will be noted that the steam supply is controlled by a float operating from the pressure at the base of the column so that this pressure is maintained constant.

It would be easy to maintain both the feed and the draw-off constant, but the composition of the feed might vary. If, with constant feed, the amount of alcohol in the feed is increased, the liquid and vapor on the plates of the column will become richer in alcohol, and since a richer liquid in the column gives more back pressure for a given steam supply to the base, the steam will be cut down and the rectifier will operate as shown in Fig. 2 until the feed is checked. Not only will the distillate be poorer alcohol, but all the excess alcohol in the feed will be lost in the slop.

The operation of the column can be made fully automatic in several ways, so that such changes in feed composition will be taken care of. One method is shown in Fig. 3. Here a double wier is placed in the distillate line so that the ratio of distillate withdrawn to distillate returned to the column as reflux remains constant (0.408 to 1 in this case), and a thermostatic control is put on the steam supply to maintain a given temperature at some point in the column. The feed is controlled by a float operated from the base of the column. This method of control insures that as long as sufficient feed is available it will be supplied at the maximum allowable rate. Of course, if less is available it will simply run to the column as supplied.

After the column has come to equilibrium under the conditions given in Fig. 3 (same feed and steam supply as shown in Fig. 1), let the amount of alcohol in the feed be increased to 15 per cent. The first effect will be an enrichment of alcohol on the plates near the feed plate. This will cause the temperature at the thermostat to drop and more steam will be

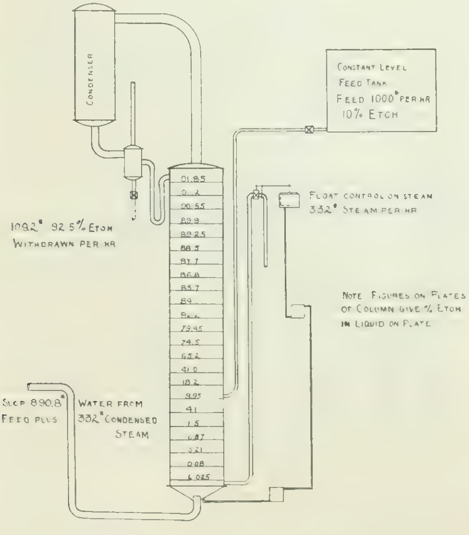

Fig. 1—Standard Continuous Rectifier

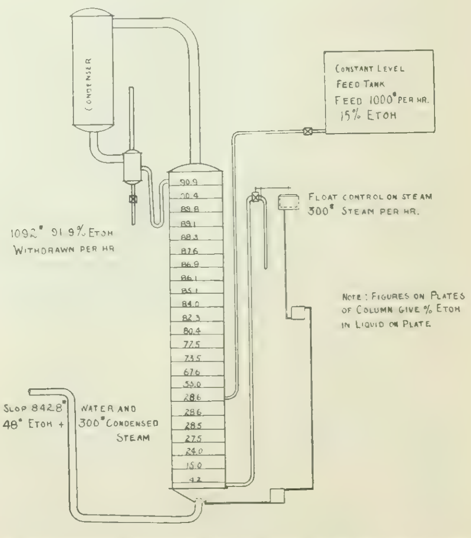

Fig. 2—Standard Continuous Rectifier with Excess Alcohol in Feed

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[1] Presented before the 15th Semiannual Meeting of the American Institute of Chemical Engineers, Wilmington, Del., June 20 to 23, 1923.

[2] This Journal, **15** (1923), 402.

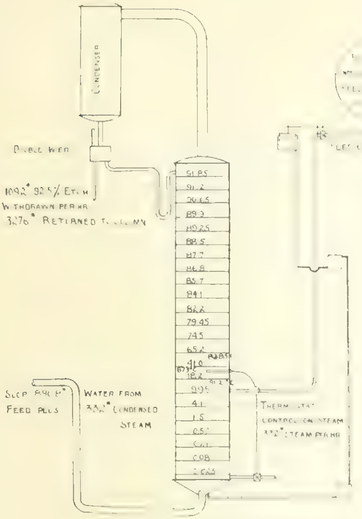


Fig. 3—Automatic Rectifier

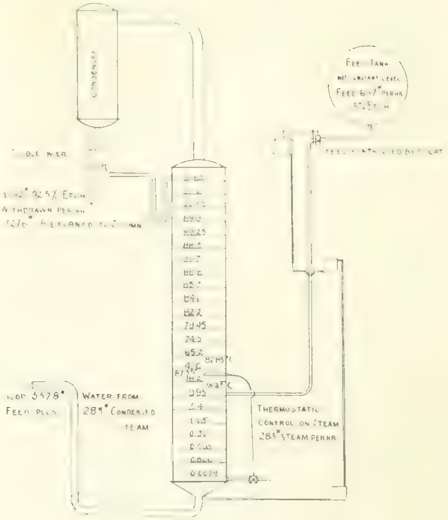


Fig. 4—Automatic Rectifier

admitted to the column. But it will also cause the pressure at the base of the column to rise, which will raise the float regulator and reduce the feed. Although the feed is richer, the column will not handle a greater amount of alcohol for the same back pressure at the base, since it should already be working very nearly to capacity at the top plates where the liquid and vapor are rich in alcohol. A very slight increase in steam will therefore start the column to load near the top and run the pressure up at the base. Hence, when a balance is finally reached, the conditions in the upper part of the column will be almost exactly the same as before the feed was changed. The conditions in the lower part of the column will be shown as in Fig. 4.

If the alcohol in the feed is reduced to 5 per cent, the column will no longer deliver 109.2 lbs. of distillate, since a much larger amount of steam is required to heat the feed. This will cause an increase of back pressure in the lower section of the column. When equilibrium is finally reached, we may be getting about 100 lbs. of distillate from 1850 lbs. of feed. The slop will run 0.21 per cent alcohol. In case it is necessary to take care of such wide variations of feed, a small addition can be made to the bottom of the column. The equivalent of five extra theoretical plates below the feed plate will bring the slop down to 0.01 per cent in this case.

It is seen that by maintaining the ratio of reflux to distillate constant, the composition of the distillate will be absolutely independent of the composition of the feed. The automatic rectifier will work just as well on many other mixtures, such as alcohol and acetone, acetone and water, ammonia and water, and it will work nearly as well on any mixture of two liquids. It has also been arranged to make separations of mixtures containing more than two components.

Variations of this arrangement have been used. For example, where it was required to keep a given amount of distillate on hand, the feed was controlled by the level of distillate in a storage reservoir. One of these units has operated for over two months without any attention whatever.

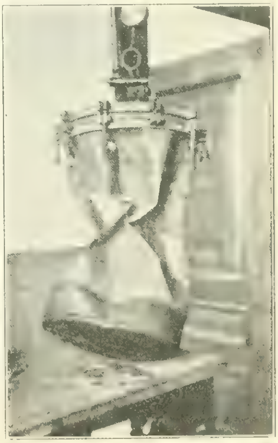
Patent applications covering this rectifier have been made.

The Collapse of the Autoclave[1]

By W. P. Mason

Rensselaer Polytechnic Institute, Troy, N. Y.

This photograph explains itself and shows what can happen to a brass, cylindrical autoclave (about 15 x 25 in.), when a vacuum is formed after steam condensation takes place. This particular apparatus has been in use for several years. It collapsed only recently.



After having been heated to 15 lbs. for 15 min., the gas flame was turned out and the autoclave was allowed to cool without opening the relief valve. It is true that if the valve had been slightly opened this collapse would not have occurred, but it is not safe to depend upon the student slowly opening the valve, and if it is opened suddenly the cotton plugs will be blown out of the vessels within the autoclave.

The design is at fault. There should be a sufficiently strong band around the middle of the cylinder to permit its withstanding a reversed pressure when the steam condenses.

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[1] Received May 11, 1923.

The Use of Lime in the Glue and Gelatin Industry[1]

By Robert H. Bogue

Lafayette College, Easton, Pa.

To UNDERSTAND properly the function of lime, it is necessary to point out briefly the several steps in glue and gelatin manufacture. Several types of raw stock are used, which include hide pieces and trimmings from the tanner or the packer; fleshings, which consist of the under layer of the hides and are made up of loosely packed fibers of skin substance, fat cells, and thin muscles attached to the skin; sinews or tendons and connective tissue; ossein, which is the organic portion of bones left behind when the mineral matter is dissolved out with acids; and bones. All of these with the exception of untreated bones are conveniently grouped together as hide stock. Since bones do not receive a lime treatment, they will be omitted from the discussion.

The hide stock is first washed to remove dirt and salt or other preserving material that may have been added, and shredded to bring a greater surface exposure to the reagents employed later. This material is then allowed to stand in vats with a suspension of lime (water-slaked) in water. After about two weeks the stock is forked out and a fresh suspension of lime in water is added. After two or three such treatments the stock will have attained a plump, uniformly swollen condition, and it is then removed and washed, first with water and subsequently with a dilute acid solution to neutralize the excess of lime. The neutralized stock is placed in a large, open tank, with water and steam admitted below a false bottom until the mixture has attained a temperature of 80° C. or higher. This operation, known as the boiling process, brings about an extraction of the gelatin. The liquor is run off after a few hours, and the boiling repeated a number of times with fresh lots of water.

The liquors may then be filtered or clarified, and, being too thin to gel well, are concentrated *in vacuo* and allowed to form a jelly, after which they are dried and ground as desired.

CHANGES BROUGHT ABOUT BY THE LIME

The most obvious changes that have been induced by the liming operation are the greatly increased volume and the loosening of the hair. The hide pieces have increased to several times their original cross section, and have taken on a firm, rigid appearance. If the hair has not actually fallen off during the lime treatment, it will be found to be held so loosely that a gentle rubbing with the fingers will suffice to remove it.

Perhaps less obvious, but of more importance, are the chemical changes involved. If raw hide pieces were heated with water, solution would be effected very slowly unless a temperature above 100° C. (under pressure) were used. But gelatin, the constituent of glue which gives it the power to form a jelly and upon which adhesiveness seems to depend, is a heat-sensitive substance, and when exposed to high temperatures rapidly undergoes a decomposition, breaking up into constituents which have very little or no value as jelly producers or adhesives. As a result of the lime treatment, however, the hide pieces are enabled to pass into solution by only a moderate heat treatment with water, and the valuable properties of the gelatin are preserved.

Just how the lime functions to bring about this result is not yet altogether clear, but it seems that the alkaline solution induces a loosening and separation of the fibers in the hide. When these are packed tightly, as in untreated skin, they present a limited surface exposure, but the distension produced by the lime offers a greater surface exposure and consequently permits a greater rapidity of solution.

ALKALI CONCENTRATION

This plumping action appears to be due to a particular concentration of hydroxyl ions or alkali. If portions of a neutral hide are immersed in water containing increasing amounts of alkali or of acid, the hide swells more as larger amounts of alkali or acid are added (there is at first a slight decrease in volume on adding acid) until a certain maximum of swelling is attained, and if still more alkali or acid are added beyond this point, the swelling becomes less and solution takes place. The alkalinity of a saturated solution of lime is very close to that alkalinity at which maximum swelling occurs.

But if only a saturated solution of lime in water is added and the alkalinity of the solution is tested at regular intervals after introducing the hide pieces, it very rapidly becomes less alkaline, and is soon almost neutral. This would also be the case with any other alkaline or acid substance, and is due to the ability of the hide to absorb or react with hydroxyl or hydrogen ions, respectively. By using a suspension of the lime in water this difficulty is overcome, for a suspension is merely a saturated solution plus an excess of the undissolved solid. As rapidly as the hydroxyl ions are removed by the hide, just so rapidly will the undissolved lime pass into solution. By this means the alkalinity of the mixture is automatically held constant. It is this property of a nearly foolproof and automatically controlled alkalinity that makes lime better than most other reagents for this service.

SOLVENT ACTION OF LIME

Besides collagen, which is converted into gelatin by heating in water, glue stock contains several other proteins that have no value whatsoever in glue. Elastin is found in the connective tissue, mucin is found in cartilage, keratin is contained in hair, and albumins are always present. If these substances were allowed to be cooked with the stock, the product would be weakened and would also give a glue that was turbid, muddy, or opaque. These proteins, especially the albumin and mucin, are soluble in alkaline solutions, and so are dissolved out of the stock by the lime. Acids would not effect such solution. Here again the lime is particularly well adapted for the purpose, as solutions of stronger alkalinity would dissolve also increasing amounts of the collagen and solutions of weaker alkalinity would not be effective in dissolving even the albumins or mucins.

As the albumins and elastin are attacked by the lime the roots of the hair become loosened, for they are embedded directly in the layer of elastin below the epidermis. The hair, having no longer any support, falls out or is easily rubbed off. Some of the fat of the stock is also acted upon by the lime, forming insoluble lime soaps that should be removed in the washing process if a clear product is desired.

GERMICIDAL ACTION

Lime itself is a very good germicide for most microbiological organisms. There are some forms of bacteria that

[1] Received October 9, 1922.

thrive in lime solutions and high counts have been obtained of these, but the putrefactive organisms are almost entirely killed or inhibited. In general, it is quite unnecessary to add other preservatives during the liming process.

Selection of the Lime

It is important to use care in the selection of the lime for hide swelling, for it has been found that dolomitic limes which contain large amounts of magnesia are decidedly inferior to the high calcium limes. For some reason that is not entirely clear, the magnesia tends to offset the normal swelling induced by the lime. In practice it is usually most satisfactory to procure a high-grade quicklime and slake it at the plant just prior to use.

The iron oxide content of the lime should likewise be low, as otherwise the color imparted by it to the finished glue or gelatin may be objectionable, and bleaching may then be necessary.

The Determination of Solids (or Moisture) by Means of a Gauze Dish[1]

By Armin Seidenberg

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The determination of solids or dry substance (moisture by difference) of viscous organic liquids is one of the most frequent operations in chemical investigations. In spite of its seeming simplicity, it has generally been found impossible to secure strictly quantitative results by any of the methods so far proposed. Pumice stone, sand, and other finely divided materials usually used as distributing media, have a tendency, after being heated, slowly to adsorb gases and liquids. The slight traces of adsorbed moisture are held very tenaciously and tend greatly to increase decomposition of solids, so that it is difficult to differentiate between the loss due to evaporation of moisture and that due to decomposition of solids. For this reason it is not possible to secure a definite end-point followed by a correct constant weight that indicates the actual solids present.

In order to secure more satisfactory results a dish of corrugated wire gauze has been proposed. This permits the liquids to be distributed over a wide surface; it also permits uniform dehydration, is unaffected by chemical action, and does not change in weight during cooling or weighing. It has no tendency to retain moisture, and largely for this reason the decomposition of the solids distributed over it has been found to be much less than is the case with pumice or sand. It is always possible with the gauze dish to secure a sharp end-point followed by a true constant weight that remains constant on prolonged heating and that indicates the correct amount of solids present. A large number of comparative determinations were made on various sugar and other solutions between the gauze dish and pumice stone methods, and very considerable differences were noted in the results by the two methods—equal in many instances to 3 per cent and more of the solids present. By using higher temperatures rapid results (in about half an hour) can be secured on many materials with the gauze dish.

THE most favorable condition for the thorough removal of the volatile portion of a liquid is a wide and uniform distribution of the liquid over a large surface which will itself remain entirely unaffected throughout the drying operation. In a previous paper[2] the writer has described a device, a modification of which was found to meet these conditions to a marked degree. This device, or gauze dish, is made from a fine mesh wire gauze with an area of 200 sq. cm., corrugated into 31 to 33 lateral ridges and compressed in this way into an area of 8.5 × 5.5 cm. The gauze dish referred to in this paper was made of platinum and rested upon a platinum-gold stand. In order to protect hygroscopic material it was placed during weighing in a closed dish made of thin, light-weight lead sheets. The drops of any liquid when delivered from a slight height (about 2 cm.) upon a gauze in this form are broken up by the impact of the fall and held entirely as a fine film within the meshes. In this way the grooves formed by the corrugations exert a capillary action and 5 cc. of any liquid can readily be distributed over the gauze dish without any going through the meshes. Owing to the large surface and to the effect of the meshes and corrugations in maintaining a wide and even distribution of the liquid, dehydration is greatly facilitated. Evaporation of the liquid takes place from both surfaces. After all the water has been removed the solids will be found to be held uniformly within the meshes, forming an integral part of the gauze dish. All dehydrations were carried on in an electric oven, those in parallel being conducted in dishes placed side by side upon a small cardboard tray.

Sucrose Solutions

Results with Pumice Stone—Several hundred parallel determinations at temperatures ranging from 55° to 175° C. were made under exactly the same conditions, by the gauze dish and pumice stone methods,[3] on sucrose solutions of varying concentrations. The pumice stone used was subjected to careful preliminary purification; it was used only after standing under atmospheric conditions for several weeks and then dehydrated in each instance in the manner recorded in the table. The pumice, before being weighed, was always placed in a desiccator for exactly 10 min.

It was found that pumice, as well as any other material consisting of finely divided particles or containing openings of capillary size, had a tendency to adsorb both gases and liquids, particularly after having been heated. Material in a colloidal state such as this is affected by the conditions of temperature and pressure so that its weight changes, not only during evaporation, but also during cooling and weighing. Considerable evidence will be presented in another paper[4] indicating that, although decomposition of organic residues distributed over pumice does not take place in the presence of a large excess of water, it is greatly accelerated by the slight traces of adsorbed moisture held throughout the dehydration by the pumice.

Radically different results were secured by the pumice stone method, dependent upon the manner in which the pumice had been dehydrated before being weighed. In those instances (No. 3, Table I) where it was first heated over the Bunsen flame, results were secured which after a

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[1] Received October 25, 1922.

[2] This Journal, **7** (1915), 769.

[3] Assoc. Official Agr. Chem., Methods, **1920**, p. 101.

[4] To be published in *J. Assoc. Official Agr. Chem.*, August 15, 1923.

TABLE I SERIES B, SUCROSE SOLUTION
Solids, calculated from specific gravity = 15.93 per cent

DISTRIBUTING MEDIUM	METHOD OF DEHYDRATING	PER CENT SOLIDS							
				Number 1a					
Time, hrs		6	20	45	2	15	32	15	....
Temperature ° C.		58	50	60	55	60	60	60	...
Pumice	4 hrs., 58° C.	16.542	16.430	16.151	16.214	16.139	16.139	16.109	...
Gauze dish	Heated to redness	16.303	16.229	15.976	15.984	15.957	....	....	..
				Number 1b					
Time, hrs		6	4	4	5	3	....	..	....
Temperature, ° C		58	55	58	60	60	...	..	...
Pressure, in.		10	25	24	25	25	....	....	...
Pumice	4 hrs., 60° C.	16.943	16.438	16.259	16.179	16.215	...	...	...
				Number 2					
Time, hrs.		3	2	2.5	4	3	2	15	75
Temperature, 99° C.									
Pumice	1.5 hrs., 100° C.	16.075	15.844	15.657	15.390	15.242	15.186	14.629	12.596
	Heated to redness	16.339	16.306	16.290	16.254	16.234	16.234	16.266	..
Gauze dish	Heated to redness	16.043	16.043	16.009	15.936	15.919	15.927	15.906	...
				Number 3					
Time, hrs.		6	3	3	3	15	....	..	....
Temperature, 100° C.									
Gauze dish	Heated to redness	16.143	15.995	15.926	15.926	15.926	....	..	....
				Number 4					
Time, hrs		2.5	1.5	2	3	3	2	15	..
Temperature, 108° C.									
Pumice	48 hrs., 117° C.	16.067	15.994	15.839	15.640	15.409	15.260	14.577	.
Gauze dish	Heated to redness	16.081	16.045	15.976	15.891	15.863	15.843	15.855	.
				Number 5					
Time, hrs.		5	4	3	3	15	3	45	..
Temperature, 112° C.									
Gauze dish	Heated to redness	16.175	15.961	15.951	15.938	15.894	15.911	15.880	..
				Number 6					
Time, hrs.		2	2	2	2	3	3	2	45
Temperature, 117° C.									
Pumice	4 hrs., 117° C.	15.803	15.430	15.151	14.919	14.674	14.436	14.297	13.522
Gauze dish	Heated to redness	16.176	16.063	15.981	.	15.924	15.918	15.912	15.884
				Number 7					
Time, hrs.		4	2	2	2	2	2	15	50
Temperature, 125° C.									
Gauze dish	Heated to redness	16.036	15.967	15.918	15.908	15.894	15.908	15.871	15.826
				Number 8					
Time, hrs.		1	2	2		..	.		..
Temperature, 148° C.									
Gauze dish	Heated to redness	15.927	15.849	15.802		.	..		....
				Number 9					
Time, hrs.		0.5	0.5	0.5	36	..			..
Temperature, 155° C.									
Pumice	15 hrs., 150° C.	26.631	14.802	14.009	12.605				.
Gauze dish	Heated to redness	15.951	15.906	15.859		.			..
				Number 10					
Time, min.		15	15	15	30	.	.		
Temperature, 160° C.		160	175	175	175	.	.		
Gauze dish	Heated to redness	16.110	15.908	15.840	15.670			.	...
				Number 11					
Time, min.		30	30	.	..	..	...	...	..
Temperature, ° C.		140–155	155	...	.	.		.	..
Gauze dish	Heated to redness	15.945	15.913	.		.	.	.	
				Number 12					
Time, min.		20	30	30	.	....	..	..	..
Temperature, ° C.		155	155	155	.	..	.	....	..
Gauze dish	Heated to redness	16.142	15.938	15.902	.	....	..	...	..

certain period remained approximately constant. However, these results were usually too high by amounts that in two series of determinations (Series A and B)[5] were 1.2 to 3 per cent of the actual dry residue. In other series of determinations even greater differences were observed, and it was generally impossible to secure satisfactory checks unless all the pumice used had previously been heated in one batch. In other words, a fictitious constant weight was attained which was usually incorrect, and which could only be correct as the result of the balancing effect of two counteracting sets of errors—one due to the loss in weight produced by the disintegration of the organic material, the other due to the gain in weight resulting from the adsorptive power of the pumice.

On the other hand, pumice dehydrated by being heated at the temperature at which evaporation is subsequently carried on (Nos. 1, 2, and 3, Table I) yields with sucrose solutions results that show a continuous loss in weight on heating. Similar results were also obtained with sand (25 to 30 g.) dehydrated at 100° C. This loss in weight is so decided and so continuous that it is not possible under these conditions to attain a sharp end-point that will clearly differentiate the completion of the evaporation of the liquid from the decomposition of the solid. This is true no matter what temperature is used for the evaporation. A lower temperature will retard the rate of decomposition of the solid matter, but it will generally reduce to about the same degree the rate at which the last traces of tenaciously held moisture are volatilized. In this way a uniform rate of loss occurs in the dry residue at a percentage above the correct percentage and continues to one indefinitely below it. While some authorities recommend that heating be continued until a uniform rate of loss is noted, it will be seen that a uniform rate of loss does not necessarily indicate the correct percentage of solid matter.

FACTORS IN DETERMINING CONSTANT WEIGHT—It is therefore possible to secure accurate and reliable results only if decomposition is reduced to a point where its effect is negligible for an extended period of time—at least 2 and preferably 3 to 4 hrs.—and where in any case the rate of loss due to this cause is decidedly less than that due to evaporation. In this respect it will be found that the gauze dish adds greatly to the reliability of the results, since it practically adsorbs no moisture and since largely for this reason the dry residue on it is not readily decomposed and there is therefore always a distinct difference in the rate of loss due to decomposition and that due to evaporation.

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[5] Results secured with Series A are similar in character to those secured with Series B and are therefore not tabulated.

Results with the Gauze Dish—Although the rate of evaporation varies with the temperature, the constant weights attained on sucrose solutions with the gauze dish, at temperatures ranging from 55° to 125° C., were in close agreement with each other and with the correct percentage indicated by the specific gravity. Furthermore, the same results were obtained with vacuum as at atmospheric pressure. In Series A, where six determinations were carried on at temperatures ranging from 57° to 117° C., the average of all constant weights secured by the gauze dish represented 23.417 per cent,[6] the percentage calculated from the specific gravity being 23.40. The average variation from this average was 0.005 per cent, the maximum 0.013 per cent. In Series B, Table I, the average constant weight on the series of determinations made on the gauze dish at or below 125° C. represents 15.930 per cent, the percentage calculated from the specific gravity being 15.93 per cent. The average variation from this average is 0.018 per cent, the maximum 0.041 per cent.

In a considerable proportion of gravimetric determinations the experimental error is considered to be about 0.02 per cent, in terms of the whole amount. In the present case, in addition to the errors due to measuring out and distributing the liquid, four independent weighings are required, which might introduce discrepancies in the final result. These would readily account for the slight differences noted and we may conclude that errors due to the incomplete evaporation of the liquid or to the decomposition of the solids even after prolonged heating may be considered as negligible when the gauze dish is used with sucrose solutions.

Results on Prolonged Heating—On heating the residues of Series A on the gauze dish for a prolonged period, the total averaging 42 hrs., an average weight representing 23.368 per cent was obtained, which differed from the average constant weight representing 23.417 per cent by only 0.049 per cent. This is equal to an average loss after constant weight has been reached of slightly more than 0.001 per cent per hr. In Series B (Table I) practically the same condition is to be noted. After an average constant weight on the determinations at or below 125° C. representing 15.930 per cent was obtained on the gauze dish, continued heating totaling an average of 54 hrs. showed an average weight representing 15.891 per cent, differing from the average constant weight by 0.039 per cent. In this instance the average loss of weight after constant weight has been reached corresponds to slightly less than 0.001 per cent per hr. These figures may be compared with those secured in Series A, where determinations in parallel with the gauze dish were run in all cases on pumice dehydrated under the conditions under which evaporation was conducted. Here after heating for an average of 42 hrs. the residues in the six determinations, which on the gauze dish equaled 23.368 per cent, equaled 21.907 per cent on the pumice stone.

The End-Point on the Gauze Dish—As has been noted, the exact point of time when constant weight has been reached can be only approximately estimated. Since on the gauze dish the rate of loss per hour of the solids on prolonged heating after the complete evaporation of the moisture is so slight that it may be considered negligible, the length of the heating period on the basis of which this is eatsblished may be extended considerably. In this way fewer weighings are usually needed to determine whether constant weight has been reached and the weighings can be arranged according to the convenience of the worker. In any case, the difference between the rate of loss due to evaporation and that due to decomposition is very much accentuated and an end-point that is quite distinctive is secured. Thus, in the curves (Fig. 1) for the gauze dish in contrast with those for the pumice, a turn occurs at the true percentage, after which the curves hardly deviate even on prolonged heating. Constant weight is therefore established with accuracy and certainty.

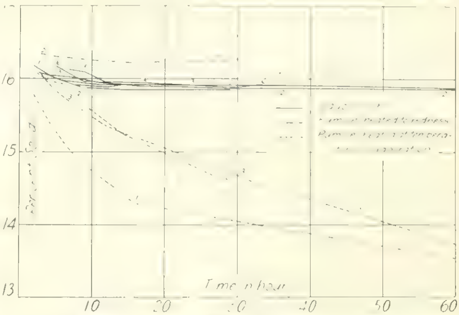

Fig. 1—Series B (99°-125° C.). Sp. Gr., 15.93 Per cent

Temperature Giving Most Favorable Results with the Gauze Dish—There is an advantage in using the highest temperature that has no decomposing effect in that the quickest results with the sharpest turning or end-points are secured in this way. At 98° to 100° C. prolonged heating is often needed to secure complete dehydration of strongly viscous material such as sucrose, particularly when the concentration is above 20 per cent. However, correct results can always be obtained with the gauze dish if the solution is not too concentrated and if the precaution is taken to distribute the material widely. At considerably lower temperatures (50° to 60° C.) required in the presence of levulose, a longer time is needed for the evaporation, but there is no tendency to retain slight traces of water and constant weight once reached is in agreement with the correct results. This is not the case with pumice, where high results are frequently obtained at low temperatures. In the absence of readily decomposable material a temperature of 120° to 125° C. is best with the gauze dish, while in the presence of material slightly more subject to decomposition a temperature of 110° C. should be used, and, as will be shown later, if the material is readily decomposable a temperature below 70° C., preferably 50° to 60° C., should be used.

High Temperature with Gauze Dish—A study of Numbers 7, 8, 9, 10, and 11, Series B, Table I, will show that at 155° C. the correct result for solids can be obtained in approximately one-half hour, and that the subsequent loss at the same temperature during half-hourly periods averages between 0.03 and 0.04 per cent. On pumice the corresponding loss per half hour was 1 per cent and the correct weight was not indicated in any way. With the gauze dish at this temperature the end-point is sharply indicated and the constant weight attained remains fairly constant, so that the results are still approximately correct within an hour after this. It is therefore possible by means of the gauze dish to secure rapid and accurate results on substances of the nature of sucrose, by using high temperatures of about 155° C. In this way results can be had in about one-half hour, and subsequent weighings to determine whether constant weight has been reached should be made at half-hour intervals.

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[6] Although the percentage figures given here and in the tables should e considered as correct only to the second decimal place, the third place in the decimals is given since in many instances the difference between the percentage figures occur in the third place and could only be indicated by showing this.

TABLE II—SERIES C, LEVULOSE SOLUTION
Solids, calculated from specific gravity = 23.02 per cent

Distributing Medium	Method of Dehydrating	Per cent Solids									
Number 1											
Time, hrs.		6	3	3	4	4		....	..	....	....
Pressure, in.		15	27	27	27	27					
Temperature, 70° C.											
Pumice	4 hrs., 70° C., 28 in.	23.017	22.796	22.619	22.563	22.469	..	.	...	...	....
	Heated to redness	23.086	23.047	22.950	22.934	22.898	.	...	..	..	....
Number 2											
Time, hrs.		6	2	4	6	3	15 min. desic.	.	..	....	...
Pressure, in.		15	29	29	28	28	....	...	..	...	....
Temperature, 70° C.											
Pumice	7 hrs., 70° C., 28 in.	23.888	22.921	22.847	22.709	22.645	22.797	..	..	....	....
Gauze dish	Heated to redness	23.090	22.887	22.855	22.758	22.730	22.730	.	.	.	....
Number 3											
Time, hrs.		4.5	2	4	4	3	3	3	3	3	4
Temperature, 70° C.											
Pumice	15 hrs., 70° C.	31.957	24.310	22.938	22.841	22.754	22.717	22.694	22.649	22.639	22.233
Gauze dish	Heated to redness	23.074	22.969	22.945	22.861	22.806	22.773	22.740	22.731	22.725	22.554
Number 4											
Time, hrs.		2	2	2	2	2	2	..	.	...	...
Temperature, 90° C.											
Pumice	3 hrs., 90° C.	28.700	22.850	22.599	22.441	22.314	22.211	...	...	..	..
Gauze dish	Heated to redness	22.946	22.760	22.664	22.581	22.519	22.484		..	.	...
Number 5											
Time, hrs.		4	2	2	2	2	3	3	3	3	....
Temperature, 50° C.											
Pumice	4 hrs., 50° C.	56.041	40.491	30.568	25.263	24.107	23.427	23.258	23.214	23.228	...
Gauze dish	Heated to redness	23.667	23.498	23.373	23.320	23.287	23.183	23.097	23.047	23.047	..
Time, hrs.		3	40	4			..	....	.	...	.
Temperature, 50° C.											
Pumice	Continued	23.164	23.009	22.985	23.063		..	.	...	..	.
Gauze dish	Continued	23.047	22.943	22.923	22.943		...		.	..	..
Number 6											
Time, hrs.		4	2	2	2	2	2	2	2	17	....
Temperature, 60° C.											
Gauze dish	Heated to redness	23.428	23.246	23.041	22.992	22.930	22.898	22.873	22.864	22.766	....
Number 7											
Time, hrs.		4	2	2	2	2	17	...	...	....	....
Temperature, 65° C.											
Gauze dish	Heated to redness	23.147	22.978	22.948	22.925	22.948	22.711	....	..	....	....
Number 8											
Time, hrs.		6	2	2	4	2	7	....	....	....	....
Temperature, 57° C.											
Pumice	4 hrs., 57° C.	24.205	23.270	23.152	23.054	22.955	22.707	....	....	....	....
Gauze dish	Heated to redness	23.268	23.132	23.068	23.027	22.956	22.768	....	....	....	....

LEVULOSE SOLUTIONS

TEMPERATURES OF 70° C. AND ABOVE—When solutions containing readily decomposable levulose were dehydrated according to the official method of the Association of Official Agricultural Chemists,[3] which requires evaporation *in vacuo* at 70° C. from pumice previously heated to redness, it was only occasionally possible to obtain results that were in agreement with those indicated by the specific gravity. In many instances, however, this was not the case. Where the pumice had been previously dehydrated by heating *in vacuo* at 70° C. (Table II, Nos. 1 and 2) there is a continuous loss in weight, and the true solid content is not indicated in any way. A similar condition exists with pumice when evaporation is carried on at 70° C. under atmospheric pressure. With the gauze dish somewhat similar results are obtained under these conditions. At a higher temperature (Table II, No. 4) the rate of decomposition is very much accelerated, slightly more so with the pumice than with the gauze dish.

TEMPERATURE GIVING MOST FAVORABLE RESULTS WITH GAUZE DISH—In order to obtain a satisfactory constant weight a lower temperature than 70° C. must be used for levulose solutions. When the gauze dish is used as the distributing medium and a temperature of 50° to 60° C. is applied, a distinct decrease is evident in the rate of loss at a point indicating the completion of the dehydration and corresponding to the true solids. The weight from this time on remains practically constant, particularly at 50° C. and it is in close agreement with the correct percentage as shown by the specific gravity. This is not equally true with pumice. At 50° C. (Table II, No. 5) the constant weight obtained with pumice is considerably too high, caused, no doubt, by the retention of moisture due to the adsorptive power of the pumice at this temperature. At temperatures slightly higher than 50° C., the results with pumice are not as high, but the actual dry residue is not definitely indicated by a sharp end-point or a satisfactory constant weight. With the gauze dish there is also a continuous loss in the case of levulose solutions at 60° C., but it is at a lesser rate than that due to the dehydration and the true solids are indicated fairly accurately. However, at 50° C. there is practically no loss in weight once the true solids are indicated, and this would therefore seem to be the most favorable temperature for determining levulose on the gauze dish.

SOLUTIONS CONTAINING BOTH LEVULOSE AND SUCROSE—In Table III are recorded the results secured on a solution (Series D) containing levulose and the more viscous sucrose in equal amounts. Owing to the presence of levulose a temperature between 50° and 60° C. must be used. It will be noted (Table III, Nos. 1, 2, and 3) that where the gauze dish is used as the distributing medium constant weights are obtained which are in fair agreement with each other and with the weight indicated by the specific gravity, and that these weights remain constant throughout a prolonged period of heating. At the same time the checks obtained are not as close as those obtained in some other instances with sucrose solutions.

It was also found that a solution containing the two sugars in equal proportion, but which was more concentrated than in the present instance, did not yield, either with the gauze dish or the pumice stone method, results showing a sharp end-point or a satisfactory constant weight. Pumice, however, did not yield correct results even with a dilute solution, as can be noted both in No. 4, Table III, where the determination was carried on according to the official method of the A. O. A. C., and in No. 1 where the pumice was previously heated at 59° C. and therefore possessed less tendency to gain weight. This accords with the results previously obtained at low temperatures on viscous material such as sucrose distributed over pumice. With the gauze dish results which are entirely correct can be obtained at a temperature of 50° to 60° C., provided only the solution is sufficiently dilute and the liquid widely distributed in a thin layer.

GENERAL ORGANIC SOLUTIONS

MOLASSES—The solids of an unrefined sample of cane-sugar molasses (Series E) that was dark brown and turbid even in a dilute solution were determined according to the official method *in vacuo* at a temperature of 70° C. on pumice previously heated to redness. A uniform rate of loss was observed after 15 hrs. heating, when the losses indicated 75.64 and 75.55 per cent of solids, averaging 75.60 per cent, in the original material. When the determinations were conducted on the gauze dish without vacuum and at temperatures of 70° and 60° C., the results for solids in the original material were 74.99, 74.91 and 74.91, 74.95 per cent, respectively, averaging 74.94 per cent. The results obtained at the two temperatures on the gauze dish were in quite satisfactory agreement, but at 60° C. the rate of loss per hour was practically negligible, showing that they indicate the correct percentage. The difference between the average results on the gauze dish and on the pumice stone amounts to 0.67 per cent, or almost 1 per cent of the actual solids present.

SIRUPS—In so-called table sirups both sucrose and levulose are present, but the proportion of levulose to sucrose is considerably greater than is the case in molasses. With the gauze dish the average solids present in the original material (Series F) were 78.57 per cent (maximum difference of 0.14 per cent). Temperatures of 60° and 70° C. but without vacuum were used. When three determinations were conducted on pumice stone according to the official method, each batch being prepared separately, considerable variations in percentage (maximum difference 1.34 per cent) were obtained so that no significant average could be established. The difference in results between the two methods varied from a minimum of 0.04 to a maximum of 1.30 per cent which latter amounted to about 1.7 per cent of the actual solids present. Both the better checks obtained with the gauze dish and the smaller loss per hour on prolonged heating prove that the results obtained with it are the correct ones.

SWEETENED CONDENSED MILK—In Series G on sweetened condensed milk the official method,[7] involving the use of 25 to 30 g. of sand, was followed on an approximately 25 per cent solution, the temperature varying from 99° to 106° C. The results obtained in six determinations varied from 82.91 to 84.20 per cent. A uniform rate of loss was to be noted at any percentage between these figures, and had the evaporation been continued for a longer period even lower results might have been obtained.

With the gauze dish two series of determinations, yielding 83.55 and 83.59 per cent, were carried on at 105° and 110° C., respectively. These results were in practical agreement and remained constant on prolonged heating. The results obtained by the sand method were about 0.6 per cent above and below those secured by the gauze dish, equal to about 0.8 per cent of the actual solids present. Rapid and satisfactory results (83.43 and 83.59 per cent) were obtained on the gauze dish at temperatures of 140° to 150° C. in 30 to 40 min.

EVAPORATED MILK—When a 40 per cent solution of evaporated milk was dehydrated according to Bigelow and Fitzgerald[8] in an ordinary dish without sand or pumice and the results were compared with those obtained with the gauze dish, the average of five determinations with the gauze dish (old modification) was 25.646 per cent, while with the ordinary dish the average was 25.503 per cent, the difference amounting to slightly more than 0.5 per cent of the actual solids present.

NATURAL MILK—Comparative determinations made on 150 samples of natural milk by the dish method (without sand or other distributing medium) and the gauze method dish (old modification) showed that with the latter the results were uniformly higher by an average of 0.08 per cent (equal to 0.7 per cent of the actual solids present).

TABLE III SERIES D, SUCROSE 50 PER CENT LEVULOSE 50 PER CENT

Solids, calculated from specific gravity = 14.53 per cent

DISTRIBUTING MEDIUM	METHOD OF DEHYDRATING	PER CENT SOLIDS			
	Number 1				
	Time, hrs	6	4	3	2
	Temperature, 59° C.				
Pumice	4 hrs., 59° C.	14.871	14.645	14.601	14.562
Gauze dish	Heated to redness	14.620	14.509	14.488	
	Number 2				
	Time, hrs.	15	4	40	6
	Temperature, 58° C.				
Gauze dish	Heated to redness	14.524	14.572	14.534	14.510
	Number 3				
	Time, hrs	19	2		
	Temperature, 65° C.				
Gauze dish	Heated to redness	14.506	14.521	....	
	Number 4				
	Time, hrs.	10	3	....	
	Pressure, in.	15	26		
	Temperature, 70° C.				
Pumice	Heated to redness	14.773	14.733		
		14.803	14.731	....	....
	Number 5				
	Time, hrs	8	2	4	3
	Pressure, in.	12	26	26	27
	Temperature, 70° C.				
Pumice	Heated to redness	14.662	14.646	14.606	14.564

DIRECTIONS FOR GAUZE DISH

The liquid should preferably be weighed by difference and distributed one drop at a time in rows running the length of the gauze dish so that no two drops touch each other, care being taken that the ridges are aligned so that no two are in contact. About 2.5 to 3 g. of the solution should be distributed in about 100 drops over the gauze dish. In the case of highly viscous solutions containing readily decomposable material requiring a low temperature, the concentration should be between 10 and 20 per cent; otherwise, a solution having a concentration between 20 to 30 per cent may be used.

In determining the solids on the gauze dish the highest temperature that will not produce decomposition should always be used. For organic solutions containing material that does not readily decompose, a temperature of 110° to 125° C., depending upon the degree to which it is affected by heat, should be used. Rapid results (in half an hour) may be obtained with substances of this nature by using comparatively elevated temperatures (140° to 155° C.). For organic solutions containing levulose and other similar substances which are readily decomposed, a temperature of 50° to 60° C., depending upon the proportion of decomposable material present, gives the best results. No vacuum is needed in any determination with the gauze dish. Hygroscopic material should be weighed in a closed dish.

The correct percentage of solids is indicated when the rate of loss per hour is uniform and at a minimum which is maintained on prolonged heating. Since at the proper temperature this loss due to decomposition is practically negligible, the heating may be prolonged well beyond the time when the evaporation has been completed. The weighings to establish the rate of loss and the attainment of constant weight should be made in intervals of 2 to 4 hrs., depending upon the temperature.

The residue upon the gauze dish can be burned or dissolved off and the gauze dish used repeatedly.

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[7] Assoc. Official Agr. Chem., Methods, **1920**, p. 231.

[8] *Nat. Canners Assoc., Bull.* **5** (1915), 14.

Preparation of Methyl Red[1]

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METHYL RED, *p*-dimethylaminoazobenzene-*o*-carboxylic acid, has become so well known in recent years that a discussion of its value as an indicator would be superfluous. It was first prepared by Rupp and Loose[2] in 1908, by diazotizing anthranilic acid in alcoholic solution, and coupling with dimethylaniline likewise dissolved in alcohol. Aside from the use of an expensive solvent, the method gives poor yields. The method given by Tizard and Winmill,[3] using aqueous solutions, is a decided improvement.

The indicator is described in various catalogs as consisting of violet crystals; yet, most of the samples examined by the author which had been imported prior to the war were steel-blue in color. It was found that the violet crystals consisted of free methyl red, and the blue crystals of the hydrochloride. The methods described below were found to give products superior both in appearance and purity to any hitherto obtainable.

Numerous small-scale experiments were made using 10 g. of anthranilic acid, which theoretically should give 19.6 g. of free methyl red. Tizard and Winmill state that the yield is almost quantitative. Following their directions, at room temperature the best yield obtainable with reagents of high purity was only about 80 per cent. By diazotizing and coupling in the cold, and allowing the reaction mixture to stand for several hours before warming, yields of about 95 per cent could be obtained.

Rupp and Loose, as well as Tizard and Winmill, use over twice the amount of hydrochloric acid theoretically necessary for the reaction. Experiment has shown that the use of the theoretical amount of hydrochloric acid gives fully as high yields of methyl red, and with greater economy of materials. It might also be mentioned that the methyl red can be precipitated with sodium carbonate in place of the more expensive sodium acetate.

Preliminary Procedure

In an earthenware jar of 35-gal. capacity, provided with a mechanical stirring apparatus, are placed 100 lbs. of water, 40 lbs. of ice, 5 lbs. of anthranilic acid, and hydrochloric acid equivalent to 2.5 lbs. of the anhydrous acid, and the whole stirred until the anthranilic acid has dissolved, when 2.5 lbs. of sodium nitrite are added. After being stirred the mixture is allowed to stand half an hour. In the meantime 4.6 lbs. of dimethylaniline are dissolved in a mixture of 30 lbs. of water, 15 lbs. of ice, and an amount of hydrochloric acid equivalent to 1.4 lbs. of the anhydrous acid. This solution is added to the diazotized anthranilic acid with stirring, allowed to stand 15 to 20 min.; then 3.5 lbs. of sodium carbonate followed by 1 lb. of sodium acetate are added gradually with stirring. It is preferable to replace a portion of the sodium carbonate with sodium acetate to avoid the risk of using an excess of the former, whereby the soluble sodium salt of methyl red is formed.

It has been found advantageous to allow this mixture to stand several hours, usually until the following morning. Steam is then introduced to raise the temperature to 40–50° C., when the mass is ready for filtering.

It is essential that a good quality of anthranilic acid be employed, and that no free nitrous acid remain in the diazotized solution. If nitrous acid is present after the solution has stood half an hour, small amounts of anthranilic acid are gradually added until the nitrous acid is consumed; this will prevent the possible formation of nitrosodimethylaniline.

The red, amorphous product is filtered on a large stoneware suction filter and washed with water. This is usually a slow procedure and it is preferable to use a filter press.

Crystallization

Steel-Blue Crystals—The amorphous methyl red is dissolved by using 2 lbs. of caustic soda in sufficient water to give a final solution of the methyl red weighing about 30 lbs. Gentle heat may be used to effect solution. The solution is then filtered.

One volume of strong hydrochloric acid and three volumes of water are heated to boiling and one volume of the filtered solution of methyl red is gradually added with stirring, care being taken that all the methyl red is dissolved. Separation of brilliant steel-blue crystals of the hydrochloride of methyl red begins at once and the size of the crystals may be regulated by the rate of cooling of the solution. After crystallization is complete, the crystals are filtered off and washed with a little 1:3 hydrochloric acid.

This method gives an excellent product, since any impurities present, such as anthranilic acid or dimethylaniline, are dissolved by the hydrochloric acid. The crystallization of the methyl red from the acid solution is almost quantitative. The yield is about 10 lbs. The sulfate of methyl red is much more soluble than the hydrochloride, so that the use of sulfuric acid for crystallization is not feasible.

Violet Crystals—Rupp and Loose dissolved the crude methyl red in acetic acid, added water until turbidity was produced, and left to crystallize. This method is difficult to control as the methyl red frequently separates as a tar-like mass. The use of glacial acetic acid gives much better results. The dry, amorphous methyl red is dissolved in hot glacial acetic acid until a strong solution is obtained. On cooling the methyl red crystallizes readily. To make a pure product it is essential to filter the hot acetic acid before allowing it to crystallize. The fumes are disagreeable and trouble is encountered by crystallization in the filter.

The crystals separating from glacial acetic acid apparently contain two molecules of acetic acid. Crystals after exposure to the air over night were heated at 105° C. for 15 min., a strong odor of acetic acid being evolved.

	Per cent
$CH_3.COOH$ found	9.84, 9.87
Calcd. for $C_{15}H_{15}N_3O_2 + 2CH_3.COOH$	10.0

The heated crystals had a golden brown color in diffused light, compared with the violet color of crystals obtained by diluting the acetic acid solution with water.

Methyl red is easily soluble in chloroform and in warm benzene and acetone, but is sparingly soluble in petroleum ether or carbon tetrachloride. If methyl red is dissolved in chloroform and petroleum ether gradually added with shaking, the methyl red separates immediately as fine violet crystals. A hot, concentrated solution of methyl red in benzene, when allowed to cool slowly, deposits crystals of the indicator having a very deep violet color. Either of these methods of crystallization are preferable to the use of acetic acid.

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[1] Received October 20, 1922.

[2] *Ber.*, **41** (1908), 3905.

[3] *J. Chem. Soc. London*, **97** (1910), 2485.

WATER-SOLUBLE METHYL RED—If the alkaline solution obtained by dissolving the methyl red in caustic soda is allowed to cool, large, reddish brown, flat plates of the sodium salt of methyl red separate. These crystals, like those of methyl orange, are readily soluble in water and entirely suitable as a titrimetric indicator after a further recrystallization. This form of methyl red has only recently become available to chemists; yet, it has the advantage of being soluble in water, while the violet and steel-blue crystals must be dissolved in alcohol.

The Determination of Urea Alone and in the Presence of Cyanamide by Means of Urease[1]

By **Edward J. Fox and Walter J. Geldard**

FIXED NITROGEN RESEARCH LABORATORY, WASHINGTON, D. C.

An accurate and direct method has been developed for the determination of urea, which is based on the conversion of urea to ammonium carbonate by the action of the enzyme urease and subsequent titration of the ammonia thus formed.

The adaptation of the method to various mixtures containing cyanamide is described, but the method appears to be of quite general application.

A brief study of the rate of conversion of urea by urease in solutions of various concentrations has been made.

AN ACCURATE method for the determination of urea was required in connection with a number of investigations at this laboratory on calcium cyanamide and its derivatives. In the method which has been frequently employed for its determination in commercial calcium cyanamide the difference between total nitrogen and the sum of cyanamide and dicyanodiamide nitrogen is considered as urea. This method does not give reliable results, for several reasons, as has been previously pointed out.[2]

Direct methods, such as precipitation by mercuric nitrate or measurement of the nitrogen liberated on treatment with sodium hypobromite,[3] are not applicable in the presence of other nitrogen compounds, which frequently occur in calcium cyanamide. The method proposed by Johnson,[4] which is based on the precipitation of urea with oxalic acid in anhydrous organic solvents, is of limited application, since it can be used only on anhydrous samples. The determination by means of xanthydrol[5] was found unsatisfactory, since in the presence of strong acetic acid cyanamide is gradually converted into urea.

From a number of investigations[6] on the action of the enzyme urease on urea and similar compounds, and on the use of this enzyme in the determination of urea in urine and blood, it appeared that a method based on the action of the enzyme might be developed which would be applicable to the determination of urea alone and in various mixtures containing cyanamide and its derivatives. A study of this possibility was therefore made, and a very satisfactory method was developed which has now been in use at this laboratory for nearly three years.

In aqueous solutions the enzyme urease converts urea into ammonium carbonate and so far as is known it is specific for urea. The ammonia thus formed can then be readily determined by titration with an acid. The enzyme was discovered in the soy bean by Takeuchi[7] about 1909, and has since been found in quite a variety of beans. It occurs principally, however, in the jack bean (*Canavalia ensiformis*), sword bean (*Canavalia gladiatum*), and soy bean (*Soja max* or *Glycine max*). According to Mateer and Marshall,[6] the jack bean contains fifteen times and the sword bean five times as much urease as the soy bean.

The enzyme is extremely sensitive to acids and alkalies. Hydrochloric acid in concentrations greater than 0.005 *N* completely inhibits its action, while sodium hydroxide in concentrations greater than 0.02 *N* also inhibits its action. Temperature greatly affects its rate of reaction, each 10-degree rise in temperature between 10° and 50° C. causing the velocity to nearly double. A temperature of 80° C. or more will destroy its activity.

EXPERIMENTAL

Several methods of preparing and preserving the enzyme have been presented by the investigators previously mentioned. The enzyme is more active, however, when freshly extracted, and for that reason it is the practice at this laboratory to prepare it each day as needed. A few grams of jack-bean flour are extracted with twenty times its weight of water for 10 to 15 min., exactly neutralized with hydrochloric acid (about 1 cc. of 0.1 *N* HCl per gram of jack-bean flour), and filtered. Ten cubic centimeters of this extract are sufficient to convert 0.1 g. urea to ammonia in less than 1 hr.

The procedure first developed consisted of adding 2 to 3 g. of jack-bean flour directly to the sample of urea in water solution, adding a few cubic centimeters of potassium acid phosphate as a buffer, digesting in a water bath at 40° C. for 1 hr., and collecting the ammonia thus formed in standard acid by aeration. The results of urea alone were fairly satisfactory, but when tried in the presence of cyanamide they were usually high. Attempts to remove the cyanamide previous to treatment with urease, without affecting the urea content, proved futile. The volume of solution after precipitating the cyanamide and subsequent removal of the excess silver, was so great, and the concentration of inorganic salts so high, that it was almost impossible to get a satisfactory determination of the urea.

As referred to later in connection with the determination of urea in the presence of cyanamide, the stability of cyanamide in aqueous solution decreases rapidly with increasing temperature, particularly in other than neutral solutions. The foregoing procedure was, therefore, modified to overcome this difficulty.

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[1] Received November 18, 1922.

[2] Pranke, "Cyanamid," **1913**, p. 22.

[3] Monnier, *Chem. Ztg.*, **35** (1911), 601.

[4] Johnson, THIS JOURNAL, **13** (1921), 535.

[5] Fosse, *Ann. chim.*, **6** (1916), 13.

[6] Mateer and Marshall, *J. Biol. Chem.*, **14** (1913), 283; *Ibid.*, **25** (1916), 297; Van Slyke and Cullen, *Ibid.*, **19** (1914), 221; Armstrong and Horton, *Proc. Roy. Soc.*, **85B** (1912) 109.

[7] *J. Coll. Agr., Tokyo*, **1** (1909), 1414.

The sample in solution was brought to exact neutrality, using methyl red as the indicator, 10 cc. of the urease solution were added, and the solution was allowed to stand for an hour at room temperature instead of at 40° C. An excess of standard 0.1 *N* hydrochloric acid was then added and the solution aerated by passing a current of air, washed free from carbon dioxide and ammonia, through the solution until all of the carbon dioxide was expelled. Five to 10 min. were found to be sufficient for this. The excess acid was titrated with standard 0.1 *N* sodium hydroxide. The acid used up is a direct measure of the urea originally in solution. Each cubic centimeter of 0.1 *N* acid is equivalent to 3 mg. of urea. This procedure necessitates the use of a neutral solution of urease, and requires that the urea be in a neutral solution free from carbonates or other substances that would affect the final titration. Results by this method are accurate to within a few hundredths of a per cent, the accuracy being limited only by the accuracy of the measurement of the reagents. For samples containing soluble carbonates it is necessary to remove the carbon dioxide previous to the addition of the urease solution. This is readily accomplished by making the solution acid, aerating as described above, and again neutralizing.

In order to determine safe limits, both as to time of digestion and quantities of urea and urease, with which to work, the following experiments were carried out:

A 250-cc. solution containing 2.5000 g. of urea was prepared. The urease solution was made from freshly ground jack-bean flour (200 mesh). Fifteen grams of flour were extracted with 300 cc. of water for 15 min., with frequent stirring, the solution neutralized with 15 cc. of 0.1 *N* hydrochloric acid, and the insoluble residue allowed to settle out. The extract was then filtered through a fluted filter paper. In this way quite rapid filtration was obtained.

Aliquots containing 50, 100, and 200 mg. of urea were pipetted into tall-form, wide-mouth bottles (capacity 100 cc.) and diluted so that when the urease solution was added the total volume was 50 cc.; 5, 10, or 20 cc. of the urease solution were then added to the various solutions, the time noted, and the reaction stopped at various intervals by running in a measured excess of 0.1 *N* hydrochloric acid solution. The sample was then aerated by passing a rapid current of air for 5 min., and the excess acid titrated with 0.1 *N* sodium hydroxide solution.

The following data were obtained, which clearly show the course of the reaction:

RATE OF CONVERSION OF UREA TO AMMONIA BY UREASE IN VARIOUS CONCENTRATIONS OF UREA

	Urea Added	Urease Added	Per cent Urea Converted Min						
Expt.	Mg.	Cc.	1	2	3	5	8	10	15
A	100	20	66.9	95.4	99.9				
B	100	10	30.0	45.0		87.0	99.3	99.9	
C	100	5		23.7		49.2	[illegible]	77.4	95.1
D	50	10	47.4	84.0	97.2				
E	200	10	17.2	28.5		56.2		79.9	96.0

Experiments A, B, and C show that the rate of reaction is dependent on the concentration of urease and that the rate for the first few minutes varies approximately as the ratio of the concentrations. B, D, and E show the effect of urea concentration.

Most salts have a depressing effect on the action of the urease. Sodium chloride in concentration of 0.25 per cent depresses the rate of reaction to about two-thirds normal, while concentration of 1 per cent depresses the rate to one-half normal. Barium and calcium chlorides completely inhibit the action of urease after the conversion is about 75 per cent complete. To determine urea in the presence of these salts, therefore, it is necessary to remove them from solution previous to the addition of the urease. This is readily accomplished by precipitating them as carbonates. The excess carbon dioxide is then removed by aeration as described above.

DETERMINATION OF UREA ALONE

As a result of the preceding experiments the following procedure has been adopted:

Weigh out a 0.5-g. sample and dissolve it in 250 cc. of water. Pipet 25 cc. into a tall-form, wide-mouth bottle of about 100-cc. capacity, add a few drops of methyl red indicator and bring to exact neutrality, using 0.1 *N* hydrochloric acid or sodium hydroxide. Add 10 cc. of neutral urease solution and let stand for 1 hr., keeping the mouth of the bottle stoppered. Add from a buret a measured excess of standard 0.1 *N* hydrochloric acid solution, insert into the bottle a glass tube with a small bulb and fine holes at its lower end, connect with the air line through a series of acid and alkali gas-washing bottles, and aerate as vigorously as possible without danger of losing some of the solution through spattering, until all the carbon dioxide is removed—from 5 to 10 min. Two or three drops of caprylic alcohol or liquid petrolatum added to the solution will prevent frothing. After aerating for 5 min., reduce the current of air and titrate the solution to exact neutrality with 0.1 *N* sodium hydroxide solution.

RESULTS OF DETERMINATION OF UREA

Urea Used Mg.	Acid Used[a] Cc.	Urea Equivalent Mg.	Per cent Recovered
50.0	16.67	50.01	100.02
50.0	16.67	50.01	100.02
50.0	16.67	50.01	100.02
50.0	16.66	49.98	99.96
20.0	6.66	19.98	99.90
20.0	6.67	20.01	100.05

[a] Since a small difference in the quantity of 0.1 *N* acid used produces such relatively large variations in the calculated result, the use of a more dilute acid would have been preferable.

DETERMINATION OF UREA IN THE PRESENCE OF CYANAMIDE

The applicability of the urease method to the determination of urea in the presence of cyanamide was determined in solutions of known urea and cyanamide content by the method just described. Since the cyanamide contained a small percentage of urea as an impurity, it was necessary to make a correction for it. The correction was determined by difference between total nitrogen and cyanamide nitrogen, and agreed with the urea nitrogen as found by the urease method. The solutions used and results obtained are shown in the following table:

Urea Added Mg.	H_2CN_2 Added Mg.	Urea in H_2CN_2 Mg.	Acid Used Cc.	Urea Equivalent Mg.	Per cent Recovered
50.0	50.0	0.18	16.73	50.19	100.02
50.0	50.0	0.18	16.73	50.19	100.02
20.0	50.0	0.18	6.73	20.19	100.05
20.0	50.0	0.18	6.73	20.19	100.05

From these analyses it is evident that the determination of urea in the presence of cyanamide is entirely reliable. The high results previously obtained by the digestion and aeration method are explained by the fact that cyanamide is partially converted to urea in the slightly alkaline medium which quickly results from the action of urease on the urea in solution. At 40° C. the conversion of cyanamide to urea is much more rapid than at room temperature. Furthermore, the solution is made much more alkaline upon the addition of jack-bean flour to the solution than it is by the addition of neutral urease solution.

DETERMINATION OF UREA IN CYANAMIDE[8]

Extract 2 g. of cyanamide with 400 cc. of water for 2 hrs., add 2 g. of anhydrous sodium carbonate to precipitate the calcium, and continue to shake for another half hour. Filter the extract through a dry filter and take 25-cc. aliquots for urea analysis. Pipet the aliquots into the bottles previously mentioned, make the solution distinctly acid with dilute hydrochloric acid and aerate until all the carbon dioxide is expelled, as shown by the sharpness of the end-point in the subsequent neutralization. Then make the solution exactly neutral, using methyl red as indicator, add urease solution, and determine urea as described above.

The reliability of this procedure is shown by the following experiment:

A sample of cyanamide was first analyzed for urea and then to 2-g. samples of the same lot were added 0.1 g. and 0.5 g. of pure urea. The results are shown in the following table:

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[8] Fertilizer material, hydrated and oiled commercial calcium cyanamide.

Sample No.	Cyanamide G.	Urea Added G.	Urea Found G.	Per cent Recovered
1	2.0000	None	0.01344	
2	2.0000	0.100	0.11328	99.84
3	2.0000	0.500	0.51284	99.88

DETERMINATION OF UREA IN PHOSPHATE MIXTURES

The method was also applied to the determination of urea in mixtures of cyanamide with acid phosphate and with calcined phosphate.

For such mixtures which contain from 1 to 4 per cent nitrogen as cyanamide, an 8-g. sample was extracted with 400 cc. of water the same as for cyanamide. The phosphate is then precipitated completely with barium hydroxide, the excess barium precipitated along with any soluble calcium salts by the addition of a few grams of sodium carbonate, the extract filtered through a dry filter, and aliquots taken for urea determination as for cyanamide.

Sample No.	Phosphate G.	Urea Added G.	Urea Found G.	Per cent Recovered
1	8 (acid)	0.1000	0.10030	100.30
2	8 (acid)	0.5000	0.50016	100.03
3	8 (calcined)	0.1000	0.10080	100.80
4	8 (calcined)	0.5000	0.50016	100.03

In addition to the various applications of the urease method as shown in this paper, the method has been very satisfactorily employed in a number of other cases and, hence, it appears to be of quite general application.

ACKNOWLEDGMENT

Acknowledgment is made to J. M. Braham for his helpful criticism and coöperation in the preparation of this paper.

Expression of Quantity of Water-Soluble Arsenic Present in Commercial Lead Arsenates[1]

By C. A. Klein and W. Hulme

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The method now used for the expression of the water-soluble arsenic content of lead arsenates is considered to be irrational, since it ignores the fact that the quantity of water-soluble arsenic present in a spraying mixture is determined, not solely by the quantity in which it is present in the arsenate as sold, but by the total quantity of the arsenic present, the latter being the factor which determines the proportions of commercial lead arsenate and water used in making up spray mixtures. It is suggested that, in order to establish a better standard of comparison between the water-soluble contents of lead arsenates of varying composition, the former shall be calculated and expressed as a percentage of the total arsenic present. It is also suggested that all analytical values shall be determined on the samples as received, but shall be expressed on the basis of dried material, and not, as is frequently the case, on the samples as received, which may be in the dry or paste form, the water content of the latter being known to vary within wide limits.

In the course of an investigation concerning the preparation and use of commercial lead arsenates for horticultural and agricultural purposes, it appeared that the systems now in use for the expression of the water-soluble arsenic contents are unsatisfactory and require modification. It is generally accepted that in order to be effective, the mixture of water and lead arsenates used for spraying must contain not less than a certain minimum quantity of arsenic, and further, owing to the injury caused to foliage by water-soluble arsenic, it is necessary to limit the quantity which may be permitted.

COMPARISON OF BRITISH AND UNITED STATES SPECIFICATIONS

The U. S. A. Federal Insecticide Act of 1910 decrees that "lead arsenate paste must not contain more than 50 per cent water or more than 0.75 per cent of water-soluble arsenic (expressed as As_2O_5), and not less than 12.5 per cent of total As_2O_5."

The limits recommended by the Ministry of Agriculture and Fisheries of Great Britain (*Leaflet* **363**) are that lead arsenate pastes shall contain not less than 14 per cent of As_2O_5 and not more than 0.5 per cent water-soluble arsenic (expressed as As_2O_5), and that the material when dry shall contain not less than 28 per cent of As_2O_5. Further, the substances other than arsenate of lead and water which may be present in the paste as sold shall not exceed 3 per cent. It is also recommended that the container shall be labeled to indicate in terms of As_2O_5 the actual percentage of arsenic present, together with the dilution required for the production of a standard spraying mixture containing 0.1 per cent of arsenic pentoxide.

A comparison of the two specifications made on the same basis is as below:

(CALCULATED ON DRY PRODUCT, ASSUMING 50 PER CENT WATER IN PASTE)

	Total As_2O_5 (Minimum) (*a*)	Soluble As_2O_5 (Maximum) (*b*)	$\frac{b \times 100}{a}$
Federal Insecticide Act, 1910, U.S.A.	25.0	1.5	6.0
Ministry of Agriculture and Fisheries, Great Britain	28.0	1.0	3.6

The following analyses show that in America and England much of the arsenate sold contains total As_2O_5 considerably in excess of that laid down as the minimum permissible quantity:

ENGLISH LEAD ARSENATE
(Determined on paste as sold)

SAMPLE	Total As_2O_5 Expressed on Dried Material %
A	33.04
B	32.93
C	31.95
D	30.53
E	32.34

The following analyses published by Robinson[2] refer to dry material:

AMERICAN ARSENATES

SAMPLE	Total As_2O_5 %
A	31.80
C	31.65
E	31.27
H	30.75
I	32.07
J	32.94
L	31.04

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[1] Received June 22, 1922.

[2] THIS JOURNAL, **14** (1922), 314.

These analyses indicate that lead hydrogen arsenate is largely replacing the normal arsenate, and the authors are in agreement with Robinson in ascribing this change to the increased killing power of the acid salt and, to some extent, to the fact that a commercial advantage lies in the preparation of such compounds by the lowering of the ratio of lead to arsenic when arsenates are sold—as should always be the case—on their arsenic content.

REASON FOR CHANGE IN METHOD OF EXPRESSION

It appears to us that in respect to the permissible quantity of water-soluble arsenic a new position has been created by this increase in the total arsenic content of commercial lead arsenates. The prevailing limits were fixed when arsenates of lower As_2O_5 content were marketed, and while the methods of expression then devised were satisfactory, it seems that modification is now necessary because of incongruities which arise. In the opinion of the authors, the water-soluble arsenic content should be expressed as the percentage of the total arsenic present, the reason for this being apparent in the following circumstances.

Spray mixture, in order to be effective as a killing agent, depends on the quantity of As_2O_5 present, and therefore the sole factor involved in making up an efficient spray is the total arsenic content of the material, the quantity of water-soluble arsenic being disregarded in this connection. Thus, of two samples of lead arsenate pastes having the following composition, Sample A would be approved under the limits of the Federal Insecticide Act, while B, containing water-soluble arsenic in excess, would be rejected.

	A %	B %
Total As_2O_5	12.5	16.0
Water soluble As_2O_5	0.7	0.8

On making up spraying mixtures from these pastes to a common killing strength of 0.1 per cent of As_2O_5, the soluble arsenic content in the two sprays would be:

From A paste	0.0056
From B paste	0.005

so that although Paste B would be rejected on paste analysis, it would produce a mixture of the same killing strength as Paste A, and, containing less water-soluble arsenic, would therefore be preferable.

SUGGESTED CHANGES

Numerous instances of this kind have been noticed and the writers believe that the only satisfactory method which will insure the maintenance of a proper ratio between the desirable As_2O_5 and the undesirable water-soluble As_2O_5 is the expression of the water-soluble arsenic as a percentage of the whole arsenic. On this basis the Federal Insecticide Act Specification would read "the total As_2O_5 present shall not be less than 25 per cent on the dry material and of the total As_2O_5 present, not more than 6 per cent shall be soluble in water."

ANALYSIS OF DRY COMMERCIAL POWDERS

SAMPLE	Total As_2O_5 %	Water-Soluble As_2O_5 %	Parts of Water-Soluble As_2O_5 per 100 Parts Total As_2O_5
C	31.64	0.04	0.12
A	31.80	0.06	0.19
E	31.27	0.06	0.19
J	32.94	0.07	0.21
H	30.75	0.12	0.39
L	31.04	0.16	0.52
I	32.07	0.17	0.53

The English specification would be similar except for the substitution of 28 per cent for 25 per cent and of 3.6 for 6 in respect to total As_2O_5 and water-soluble As_2O_5, respectively. This basis of comparison has the advantage of placing a referee analyst in a more satisfactory position when called upon to deal with samples which are on the border line.

The following analyses of Robinson, and calculated by the writers on this basis, are submitted as illustrating the method of expression:

Their experience has shown the confusion which occurs owing to the expression of analytical results on the basis of paste containing water, and in view of the difficulties of sampling and irregularities due to evaporation, they suggest that a more satisfactory basis of comparison for materials like lead arsenate pastes is to be found in the expression of all results on the dried material, a course which will be conducive to more general accuracy and agreement. The wide difference between the limits of soluble arsenic permitted in sprays made from materials conforming with the two specifications under discussion, is worthy of note, and it would be interesting to know whether these limits have been fixed in their respective countries by field tests or on what other ground they have been determined.

Further Tests on Chlorine as a Preventive of Influenza[1]

By Harrison Hale

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Tests were made at the University of Arkansas from February 22 to March 2, 1923, on chlorine as a preventive of influenza. The conditions were similar to those in former tests made in February, 1920.[2]

Nearly 300 faculty members, students, and others took approximately 900 treatments, which consisted in breathing for 5 min. daily air containing a small amount of chlorine.

The number of cases of influenza in the college dormitories during this period was at the rate of 133 per thousand. Among all those taking the treatment, some of whom came only once, the rate was 44 per thousand. This figure included those who stated that they were sick at the time treatment was taken, as well as those who took only one or two treatments and developed influenza some days later. Omitting such cases, the rate among those taking the treatment was 13 per thousand, or about one-tenth of the average rate.

These results agree with those obtained in our previous tests.[2] They are also in accord with reports made by Gudeman[3] and by Baskerville.[4] All this suggests the possibilities of the use, not only of chlorine, but also of other gases against influenza and similar diseases. Would not exhaustive research upon this subject carried on under rigid medical and bacteriological control be decidedly worth while?

The minimum amount of chlorine needed for protection, how long this protection lasts, and the best method of treatment are all unknown. Tests have usually been made with air containing small amounts of chlorine, but Gudeman[5] found vaseline containing 1 per cent chloride of lime very efficient when "taken through the nose."

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[1] Received March 13, 1923.

[2] THIS JOURNAL, **12** (1920), 806.

[3] *Ibid.*, **12** (1920), 376.

[4] *Ibid.*, **12** (1920), 293.

[5] Personal letter, August 5, 1920.

Please Sign

The editor occasionally receives some comment or inquiry without any indication whatever as to its source. Usually, something should be said in reply to the correspondent, who is at least entitled to thanks for his trouble in addressing us. We profit from correspondence with our readers, and assure them that whatever they care to say to the editor will carry more weight if accompanied by a name and address.

An Early Type of Chemical Slide Rule[1]

By J. A. Gunton

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AMONG the treasured heirlooms of the library and museum of Transylvania College there exists a simple piece of chemical apparatus, dating from the early days of chemistry in America, which may be as interesting to others as it is to the author of this description. It is entitled, "An Improved Scale of Chemical Equivalents," by Lewis C. Beck and Joseph Henry, Albany, 1828, 2nd Edition—and is particularly illuminating with respect to the inorganic nomenclature and atomic weights of that period.

The scale itself consists of a flat piece of wood about 19 inches long and 2.5 inches wide, fitted with a sliding portion, as is the ordinary slide rule, so that the numbers on the slide may be placed opposite the names of the elements or compounds along either side of the slide. The face of the rule is covered with paper on which is printed the names of the elements and compounds that may be considered in the computations. On the back of the rule is a description of the scale and its construction. The printing on both sides is in good state of preservation and quite readable.

The mathematical construction is such that the slider of the scale is graduated into divisions and subdivisions continually decreasing in length from 8 at the top to 330 near the bottom. These divisions correspond in relative lengths to the differences of the "logarythms" of the numbers placed opposite them.

Now since the division of numbers is performed by taking the difference of their logs, and since the several divisions on the scale represent the difference of the logs of the numbers placed opposite them, it follows that the distance between any two numbers will be equal to the distance between any other two that give the same quotient by division. But numbers which give the same quotient have the same ratio to each other, therefore equality of ratio on the scale is expressed by equality of distance.

The chemical explanation of the scale may best be given in the designers' own words as printed on the back:

> The application of the logametric scale to Chemistry is founded on the most important fact in this science; Which is, *that all bodies whether simple or compound that enter into chemical combination, always unite in weights or in multiples of weights that have the same ratio to each other.* And as these relative weights have the same effect in forming neutral compounds and in producing other changes they are called the chemical equivalents, and may be expressed in numbers referable to a common standard taken as unity. (These have been called the Atomic weights, because philosophers have supposed that in all cases of chemical combination an union takes place between the ultimate atoms of bodies. This is the basis of the Atomic Theory.) On this scale the least combining quantity of hydrogen is taken as the unit; and as eight times as much oxygen enters into combination with hydrogen to form the chemical compound water, oxygen will be expressed by 8 and water by 9. If therefore the slider be placed so that 8 near the top of it coincides with the upper oxygen, the whole scale becomes a synoptical table of these chemical equivalents, having hydrogen as their radix. Thus 16 is the equivalent for Sulphur, 17 for Ammonia, 70 for Barium, 110 for Silver, etc. These substances were placed opposite the respective numbers on the slider as they have been determined by Thomson, Brande, and other approved authors.

There are included in the list of substances 36 elements and 144 compounds on which calculations may be based. Some of the terms that may be of interest are: "Bi-hydruret of phosphorus, Deut. Oxide Hydrogen, Phosphuret calcium, Muriate of ammonia, Protoiodide mercury, Bi per sulph. copper and 2nd chloride tin."

As an example of the way in which the slide rule may be used, we may take the case of carbonate of lime. Without moving the slider, the scale shows us that the equivalent weight is 50, and as this substance consists of carbonic acid and lime we find the equivalent of the former to be 22 and of the latter to be 28. The proportion of these ingredients in 100 parts can be determined by placing the slider so that 100 is opposite carbonate of lime. Then it will be noticed that carbonic acid is opposite 44 and lime opposite 56, which are the proportions of these substances in 100. Again, suppose we wish to ascertain the constituents of 100 parts of ammonium nitrate. If we move the slider so that 100 is at nitrate of ammonia, which we find has 1 W before it, indicating one proportion of water, then 1 water on the scale is opposite 11.3 on the slider, ammonia is opposite 21.2, and dry nitric acid opposite 67.5. The percentage composition of ammonium nitrate is, therefore, water 11.3, ammonia 21.2, and dry nitric acid 67.5—totaling 100.

The designers claim no originality, stating that the invention is due to Dr. Wollaston and that it is stamped with his accuracy and ingenuity. Wollaston's scale was devised in 1814,[2] after he had calculated the equivalent weights of 12 elements and 45 compounds[3] from the analyses, mostly by other men, of many compounds. Practical convenience was his sole guide and he thought that the term "equivalent weight" was less theoretical than the term "atomic weight." The original instrument was referred to by Thomson in 1817[4] as Wollaston's "sliding rule of chemical equivalents so precious in every point of view to the practical chemist." The scale of Beck and Henry differs from the original in the assumption of hydrogen as the radix or unity, which is of course an advantage in that it does away with fractional quantities. Also, in order to diminish the length of the scale and render it more portable, it commences with oxygen 8 instead of hydrogen 1, and 10 atoms of hydrogen are placed opposite 10 on the slider. For the same reason 2 of carbons, the weight of one atom of which is 6, are placed opposite twelve.

The author has been unable to find any reference in the literature of the period to this revised form of Wollaston's scale, and no record can be located with respect to its history in connection with Transylvania. About 1830, sums of money, enormous for those days, were being spent on books and apparatus, and it may have been included in these purchases. Any information with respect to either point will be appreciated.

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[1] Received March 16, 1923. Presented before the Section of History of Chemistry at the 63rd Meeting of the American Chemical Society, Birmingham, Ala., April 3 to 7, 1922.

[2] Pattison Muir, "History of Chemical Theories and Laws," John Wiley & Sons, Inc., **1909**, p. 91.

[3] *Phil. trans.*, **1814**, Part I, 1.

[4] "System of Chemistry," 5th Ed., **3** (1817), 18.

Dr. Wiley Honored

Harvey W. Wiley, president of the United States Pharmacopeial Convention, 1910 to 1920, has been elected an honorary member of the Pharmaceutical Society of Great Britain. This society, like the United States Pharmacopeial Convention, is charged with the duty of keeping the Pharmacopeia up to date. On June 7, 1923, he also had an honorary degree of Master of Arts conferred upon him by the Hahnemann Medical College and Hospital of Philadelphia, at its seventy-fifth annual commencement exercises. On June 20, Dr. Wiley went to Cambridge, Mass., to participate in the festivities in connection with the fiftieth anniversary of his graduation from Harvard University.

The Preparation of Standard Cotton Cellulose and the Proposed Methods of Analysis

Report of the Committee of the Division of Cellulose Chemistry of the American Chemical Society

The accompanying reports represent the work carried out by the committee at the request of the Division of Cellulose Chemistry.

With regard to Report I—"Preparation of Standard Cotton Cellulose," the method described has been accepted by the division as standard procedure. The committee desires to express its hearty thanks to W. O. Mitscherling, of the Hooper Mfg. Co., Baltimore, Md., for his valuable help in this connection, and to thank this company for its kindness in giving him the necessary facilities.

Concerning Report II—"Proposed Methods of Analysis," the Division of Cellulose Chemistry desires that this report be given careful consideration by those interested.

Any objections or criticisms are to be discussed fully at the Milwaukee meeting, where it is hoped the report may be presented for final action.

REPORT I THE PREPARATION OF STANDARD COTTON CELLULOSE[1]

Raw Material

It has been customary in scientific research work on cellulose to consider absorbent cotton or filter paper as pure cellulose, but this has led to numerous misunderstandings and discrepancies in analytical data, owing to the fact that the various authors do not state the method of purification employed or the source from which the cellulose was derived. In view of these difficulties, it is considered advisable to prepare, according to specific standard methods, an extremely pure cellulose which will be available for research work so that the various investigators may have the assurance that they are dealing with identical, well-defined products. As the raw material for the preparation of standard cotton cellulose, it has been found from the investigations on this subject carried out in the laboratories of the James P. Hooper Manufacturing Company, that American cotton is quite as satisfactory for this purpose as Egyptian Macco cotton (thus confirming and amplifying the work of Schwalbe as outlined in the dissertation of his pupils, Robinoff and Bay).

It is well known that raw cotton selected from various lots from the same location will, on purification, vary somewhat in physical and chemical characteristics, due to slight variations in the plant species and conditions of growth, but this variation is so slight that it may be considered negligible.

Selection of Raw Material

Since the properties of cotton fiber vary with location, it is necessary first to select the latter and then so to standardize the purification that the resulting product can be regarded as "standard cotton cellulose"—viz., a material obtained from a natural cotton of very high purity, treated by processes admittedly not severe enough to bring about any fundamental change in the constitution of the cotton cellulose, yet sufficient to yield a cotton cellulose of high purity.

Procedure

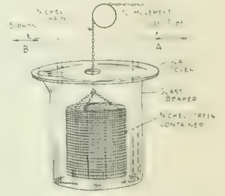
The following method is proposed as a standard procedure for the preparation of a "standard cotton cellulose:"

Mechanically clean 100 g. of Wannamaker's Cleveland raw cotton by removing the seeds and other "visible" impurities by hand-picking. Boil for 4 hrs. with 3000 cc. of a solution containing 30 g. sodium hydroxide and 15 g. rosin in a large glass vessel provided with a cover fitted with a small hole in the center, as shown in the accompanying sketch. Place the cotton loosely in a nickel-screen container, to which a small nickel chain passing through the hole in the center of the cover of the glass vessel is attached.

The process, which is a slight modification of that of Robinoff,[2] is carried out as follows:

Raise the rosin-soap solution to the boiling point, then place the nickel-screen container holding the cotton in the vessel, draw the chain through the center of the cover, and attach to a mechanical stirring device giving a direct, vertical, up-and-down movement. Operating in this manner, the cotton is neither exposed to the oxidizing action of the atmosphere nor to the danger of superheating from contact with the bottom or sides of the vessel. Boil for 4 hrs., and then remove the brown alkaline solution by displacing with hot distilled water until the wash water is only slightly alkaline.

Heat for 15 min. with an additional 3000 cc. of caustic soda solution containing 5 g. sodium hydroxide in 3000 cc. of boiled water, and remove the liquid by displacement with hot distilled water. By this means the bulk of the rosin is removed. Treat the cotton again for 10 min. with 3000 cc. of boiling dilute caustic soda containing 3.0 g. sodium hydroxide by weight, and again replace the caustic solution by hot water. During the whole process the cotton must not come in contact with air. Dump the cotton from the nickel-screen container into cold water in a large glass beaker and allow to cool in this liquid to 18° to 20° C., in order to avoid surface changes. Drain the cotton and then bleach it by immersing in 3000 cc. of a sodium hypochlorite solution (available chlorine content = 0.1 per cent chlorine) contained in a glass vessel, the solution being maintained at 20° C. and prepared as indicated in the appendix. Carry out the operation in diffused light and after standing for one hour rinse the cotton by washing on a Büchner funnel with distilled water for 10 min., repeating the operation three times. During the last rinsing add a saturated solution of sodium bisulfite drop by drop until iodo-starch paper is no longer colored. Rinse the cotton again with distilled water on a Büchner funnel, and dry by folding in linen cloth surrounded by high-grade filter paper and subjecting to hand pressure, leaving the material for several days in a room where no fumes can affect it. Thus prepared, it contains a very small trace of fat, which may be removed by extraction with alcohol-benzene mixture, but which is so slight as to be considered negligible.



A Represents Bent Glass Tube through Which the Wash-Water Is Added to Displace the Liquid B Is a Siphon. A and B Are Removed when Cellulose Is Boiled

Appendix

Selection of Raw Cotton—This should be Wannamaker's Cleveland early short staple cotton, as grown at the Model

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[1] By the term "standard cotton cellulose" is meant a very high-grade cotton cellulose, purified by a process in which, as far as possible, a minimum chemical change in the cellulose itself is brought about. The purity is defined with reference to the following constants: ash, nitrogen, cellulose number, copper number, hydrolysis number, cellulose, furfural; and cellulose number, copper number, and hydrolysis number of the isolated cellulose, as determined by the standard analytical methods adopted by the Division of Cellulose Chemistry of the American Chemical Society.

[2] Dissertation, Darmstadt, **1912**.

Seed Farm, St. Matthews, S. C. The "visible," or mechanical, impurities are to be removed by hand.

APPARATUS—The apparatus is illustrated in the accompanying sketch and is constructed of nickel screen and Pyrex glass. Used in the manner described above, the cotton is thoroughly protected from discoloration arising from atmospheric influence, as well as from local superheating due to contact with the sides of the container.

CAUSTIC SODA SOLUTIONS—These are prepared by the use of recently boiled distilled water.

ROSIN SOLUTION—This is prepared from a high-grade rosin of very low ash content, and is introduced since experience has shown that the presence of sodium rosinate naturally facilitates the removal of the fats and waxes, and also, to a certain extent, brings about a softening of the fiber.

PREPARATION OF SODIUM HYPOCHLORITE SOLUTION—The chlorine gas is obtained from compressed electrolytic chlorine. Dissolve 480 g. of pure caustic soda in 8 liters of air-free water and bubble chlorine gas slowly into the solution until a test with phenolphthalein solution indicates a neutral reaction. Carry out the experiment in diffused light and keep the solution at 0° to 20° C. during the entire reaction. (This operation is best performed by saturating the solution over night, the chlorine cylinder being kept in a water bath maintained at 15° to 20° C., and a safety bottle being placed between the cylinder and absorption flask to avoid any danger of contents being drawn back into the liquid chlorine.[3])

ANALYSIS OF "STANDARD CELLULOSE"—The following determinations should be made according to the standard methods adopted by the Cellulose Division of the AMERICAN CHEMICAL SOCIETY (and based on the bone-dry material, the moisture being determined by drying the material to constant weight at 105° C.).

1—Ash
2—Nitrogen
3—Cellulose number
4—Copper number
5—Hydrolysis number
6—Cellulose
7—Yield of furfural
8—Cellulose number copper number, and hydrolysis number of the isolated cellulose

ANALYSES OF VARIOUS AMERICAN COTTONS

By W. O. MITSCHERLING

SEA ISLAND—This variety does not give linters, and is very adaptable for the production of a standard cellulose; however, it is not a dependable source. The commercial Sea Island production has been so reduced in recent years by the ravages of the boll weevil that it cannot be recommended. Upland varieties are less pure (10 samples).

WANNAMAKER'S CLEVELAND—Breeders: The Model Seed Farm, St. Matthews, S. C.

This cotton is a medium size boll and early short staple. It is very pure and can be safely recommended for the production of a standard cellulose (10 samples).

LONE STAR—This is a Texas big boll variety, having a staple length of from $1^1/_{16}$ to $1^1/_9$ in. (10 samples).

ACALA—Acala is a Mexican early long staple. It has been acclimatized in the United States, and has a staple of $1^3/_{16}$ in. (10 samples).

The following table gives sufficient comparison of the various cottons produced in the different sections of the cotton belt:

	PER CENT		
	(1)	(2)	(3)
Sea Island			
Cellulose	86.79	85.91	89.62
Ash	1.34	1.24	1.11
Loss in bleach based on cellulose	0.61	0.60	0.64
Cuticular matters	0.81	0.82	0.89
Fats and wax	4.75	5.00	4.25
Wannamaker's Cleveland			
Cellulose	89.55	90.45	89.35
Ash	1.10	1.00	1.09
Loss in bleach based on cellulose	0.51	0.43	0.59
Cuticular matters	0.71	0.69	0.72
Fats and wax	4.10	4.08	4.00
Lone Star			
Cellulose	90.00	89.09	89.19
Ash	1.20	1.11	1.27
Loss in bleach based on cellulose	1.00	1.10	0.97
Cuticular matters	0.72	0.69	0.70
Fats and wax	4.12	4.00	4.13
Acala			
Cellulose	91.40	89.44	90.11
Ash	1.14	1.00	1.72
Loss in bleach based on cellulose	0.96	0.61	0.84
Cuticular matters	0.76	0.71	0.71
Fats and wax	4.27	4.21	4.32

From these analyses it can be seen that the different varieties are reasonably pure and uniform. The samples were shipped in three different lots. Each lot was analyzed separately, and the average analysis is given above. It may be of interest to know that the hygroscopic moisture averages 6 to 8 per cent.

All samples were purified by the process as submitted before. Ten purification tests were made for each variety (see table below).

It is very difficult to wash long staple varieties, and in purification particular care must be taken to place the cotton very loosely in the purification apparatus, otherwise it is quite impossible to wash out caustic without addition of acid, which is, of course, incorrect.

Concerning activity, or better expressed, reactivity, to form esters, the long staple is not so adaptable, and difficulties arise in getting desired viscosities unless the purified cotton is again treated in a kier under pressure with a 2 to 3 per cent NaOH solution and about 0.28 per cent Na_2CO_3 for about 10 to 15 hrs. under 40 lbs. pressure.

	PER CENT									
	(1)	(2)	(3)	(4)	(5)	(7)	(8)	(9)	(9)	(10)
					Sea Island					
Cellulose	99.30	99.41	99.52	99.21	99.56	99.61	99.43	99.41	99.60	99.10
Nitrogen	....	....	....	....	....	....	....	....	....	....
Fat					Slight indication					
Cellulose number	0.29	0.31	0.28	0.32	0.34	0.30	0.30	0.29	0.32	0.34
Corrected copper number	0.28	0.27	0.26	0.29	0.27	0.30	0.31	0.28	0.31	0.32
Copper hydrolysis number	3.01	3.00	2.98	2.45	2.76	2.64	3.10	2.95	2.91	2.96
Ash	0.08	0.09	0.05	0.09	0.09	0.08	0.09	0.07	0.07	0.09
					Wannamaker's Cleveland					
Cellulose	99.41	99.52	99.52	99.56	99.61	99.62	99.13	99.57	99.62	99.47
Nitrogen					None					
Fat					No indication					
Cellulose number	0.26	0.29	0.32	0.31	0.34	0.27	0.25	0.27	0.29	0.31
Corrected copper number	0.28	0.31	0.30	0.30	0.32	0.28	0.26	0.26	0.26	0.30
Copper hydrolysis number	2.91	2.81	2.65	2.78	2.69	2.87	2.72	2.84	2.87	2.77
Ash	0.10	0.09	0.08	0.09	0.09	0.09	0.10	0.10	0.15	0.10
					Lone Star					
Cellulose	99.30	99.25	99.31	99.37	99.27	99.31	99.31	99.61	99.34	99.64
Nitrogen					None					
Fat					No indication					
Cellulose number	0.30	0.28	0.29	0.31	0.29	0.28	0.28	0.27	0.30	0.29
Corrected copper number	0.34	0.30	0.29	0.31	0.34	0.29	0.27	0.31	0.30	0.30
Copper hydrolysis number	2.97	2.84	2.83	2.81	2.71	2.56	2.69	2.79	2.49	2.99
Ash	0.12	0.10	0.11	0.12	0.10	0.09	0.12	0.12	0.14	0.08
					Acala					
Cellulose	99.00	98.40	99.10	99.04	99.00	89.41	99.00	98.47	98.91	98.91
Nitrogen					None					
Fat					Slight indication					
Cellulose number	0.42	0.49	0.39	0.37	0.36	0.37	0.41	0.39	0.29	0.36
Corrected copper number	0.50	0.48	0.36	0.37	0.32	0.31	0.42	0.38	0.27	0.37
Copper hydrolysis number	3.14	3.07	3.09	3.09	3.07	3.04	3.00	3.16	3.09	3.07
Ash	0.21	0.18	0.17	0.09	0.07	0.09	0.10	0.24	0.12	0.23

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[3] For further information on the preparation of bleaching solutions reference is made to Matthews' "Bleaching and Related Processes," **1921**, p. 532.

REPORT II—PROPOSED METHODS FOR THE ANALYSIS OF STANDARD COTTON CELLULOSE

ASH

Place about 5 g. of cotton (accurately weighed) in a platinum dish of 98 to 100-cc. capacity, and heat gradually so as to char the substance and to avoid rapid evolution of gas. Cool, add 5 cc. of hydrogen peroxide, warm gently on the steam bath until all moisture is removed, and then ignite in a muffle or over a burner at a dull red heat. Cool the dish and its contents in a desiccator and weigh.

BIBLIOGRAPHY—(*a*) Griffin, "Technical Methods of Analysis," p. 364.

(*b*) Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, Revised to 1919.

(*c*) Lunge-Berl, "Chemisch-technische Untersuchungsmethoden," Vol. 1 (6th Ed.), p. 290.

Note: According to Griffin, digestion of relatively small samples of cotton with pure nitric acid, followed by incineration at red heat, may give low results.

NITROGEN

Dissolve 3.5 g. of snipped cotton in concentrated sulfuric acid (25 cc.) in a Kjeldahl digestion flask. Add 10 g. of anhydrous sodium sulfate (using C. P. nitrogen-free reagent) together with 0.1 to 0.3 g. of powdered copper sulfate. Conduct the heating carefully and use pumice so as to avoid bumping. Finally, heat at the boiling point until the digestion is complete and the solution is nearly colorless. Allow the mixture to cool, dilute the solution with about 200 cc. of cold water, cool again, and carefully add an *excess* (50 to 70 cc.) of saturated sodium hydroxide solution. This reagent should be added so as to avoid mixing with the acid solution. Then immediately connect the flask with a Kjeldahl bulb, which, in turn, should be connected with a suitable condenser. Agitate the flask and distil into 50 cc. of a standard 0.1 *N* sulfuric acid (or hydrochloric acid) solution containing 0.5 cc. of methyl red indicator. At least 150 cc. of distillate should be collected. Then titrate the distillate with 0.1 *N* sodium hydroxide solution and calculate the nitrogen.

The method is practically identical with the Gunning method, clearly described in the Methods of Analysis of the Association of Official Agricultural Chemists (1919), pages 5 to 8, and this book should be consulted for the details of the method.

FURFURAL

PREPARATION OF PHLOROGLUCIN SOLUTIONS—Dissolve a small quantity of phloroglucinol in a small amount of acetic anhydride, heat almost to boiling, and add a few drops of concentrated sulfuric acid. A violet color indicates *diresorcin.* If more than a faint coloration is obtained the phloroglucinol is purified as follows: Heat 300 cc. of hydrochloric acid (sp. gr. 1.06) and add 11 g. of the commercial phloroglucinol in small quantities at a time, stirring constantly until the phloroglucinol has almost completely dissolved. Pour the hot solution into a sufficient quantity of the cold hydrochloric acid (1.06) to make the volume 1500 cc. Allow it to stand at least over night, preferably several days, to permit diresorcin to crystallize. Filter immediately before using. (Yellow tint does not interfere with its usefulness.) This is the phloroglucinol reagent. It is inadvisable to prepare a quantity of the solution greater than is required for immediate use.

APPARATUS—A 500-cc., round-bottom, short ring-neck flask (approximate dimensions 150 mm. height over all and inside diameter of neck 27 mm.) with a 2-hole rubber stopper. Through one hole of the stopper a long stem, cylindrical funnel with glass stopcock is adjusted so as to reach about half-way into the flask. Through the second hole extends a distilling tube of 6 mm. inside diameter. The top of the bend is 45 mm. above the top of the flask and the tube is connected with a Liebig condenser with about a 35-cm. long jacket.

OIL BATH—Cottonseed oil has been found satisfactory, but the oil should be renewed before becoming too thick and impairing the circulation.

DETERMINATION—Place 5 g. of snipped cotton in the flask together with 100 cc. of 12 per cent hydrochloric acid (sp. gr. 1.06) and several pieces of recently heated pumice stone. Place the flask on the oil bath connect to a condenser by means of the distilling tube, and heat to 160° C., regulating so as to distil over 30 cc. in about 10 min. The distillate should pass through a small filter paper. Replace the 30 cc. distilled by a like quantity of dilute acid added by means of dropping funnel passing through the stopper. Continue the process until the distillate measures 360 cc. To the total distillate add gradually a quantity of phloroglucinol reagent (in 12 per cent hydrochloric acid of above) and stir thoroughly. The amount of the phloroglucinol added should be double that of the furfural expected plus 0.15 g. The mixture passes through yellow and green color changes, and finally an amorphous greenish precipitate should appear, which grows rapidly darker and finally becomes almost black. Make up the distillate to 400 cc. volume, allow to stand over night, and filter on a tared Gooch crucible (previously dried and weighed in a weighing bottle) having an asbestos mat. Wash carefully with 150 cc. water so that the water is not completely removed from the crucible until the very last. Then dry for 4 hrs. at 100° C., cool, and weigh in a weighing bottle. Determine the weight of the furfural phloroglucide. To calculate the furfural, pentose, or pentosan from this weight use the formulas given by Kröber.

The method is the one given in Methods of Analysis of the Association of Official Agricultural Chemists (1919), p. 96, and includes the purification of phloroglucinol. Kröber's tables on page 332 may also be used.

KRÖBER'S FORMULAS

	Weight of Phloroglucide Less than 0.030 G.	Weight of Phloroglucide 0.030 to 0.300 G.	Weight of Phloroglucide Exceeds 0.300 G.
Furfural......................	$(a^* + 0.0052) \times 0.517$	$(a + 0.0052) \times 0.5185$	$(a + 0.0052) \times 0.5180$
Pentoses......................	$(a + 0.0052) \times 1.017$	$(a + 0.0052) \times 1.0075$	$(a + 0.0052) \times 1.0026$
Pentosan	$(a + 0.0052) \times 0.8949$	$(a + 0.0052) \times 0.8866$	$(a + 0.0052) \times 0.8824$

* *a* equals weight of phloroglucide actually found.

COPPER NUMBER, CELLULOSE NUMBER, HYDROLYSIS NUMBER (SCHWALBE'S METHOD)

APPARATUS—A 1500-cc. flask with round bottom and wide, low neck, supported by a wire gauze resting on a tripod; a burner with attachment for distribution of the flame; a gas condenser fitting into the neck of the flask and suspended by a nickel wire. The center of the condenser forms a tube into which extends a glass tube of sufficient dimensions to permit a free rotation of the stirring rod of about $^1/_4$-in. thickness. This tube has an inlet on the side through which solutions can be added without removing the condenser. The lower end of the stirring rod is bent so as to form an effective stirrer and the upper end is attached to a metal tube which moves in a bearing and carries a motor-driven pulley.

PREPARATION OF FEHLING'S SOLUTION—*Rochelle salt solution:* 692 g. C. P. Rochelle salt and 200 g. sodium hydroxide, purify with alcohol, dissolve in water and make up to 2000 cc. Filter through the solution asbestos conveniently placed on a perforated porcelain plate resting in a glass funnel. Avoid contact with rubber, cork, or similar organic substances.

Copper sulfate solution: Dissolve 136.6 g. C. P. copper sulfate in distilled water, make up to 2000 cc., and filter.

Keep the two solutions in separate bottles. It is important to test the quality of the Rochelle salt in a blank test, as it has been found that this salt at times causes a precipitate of copper, presumably due to the presence of varying amounts of oxalate. The blank test is made by adding a hot mixture of 50 cc. of the Rochelle salt-alkali solution and 50 cc. of the copper sulfate solution to 400 cc. of boiling distilled water, and boiling for 15 min. in the flask under constant stirring. The solution should not assume a greenish shade, nor should any precipitate appear.

Make all determinations with air-dry material, determining the moisture content in a special sample.

DETERMINATION OF COPPER NUMBER—Place about 3 g. air-dry cotton (accurately weighed) in the 1500-cc., round-bottom flask with 250 cc. distilled water, and heat under continuous stirring to the boiling point. Simultaneously, heat separately to boiling 50 cc. of the Rochelle salt solution and 50 cc. of the copper sulfate solution in Erlenmeyer flasks of 200-cc. capacity. As soon as the water in the large flask boils add hot copper sulfate solution to the hot Rochelle salt solution and pour the mixture through the attached funnel into the round-bottom flask. Rinse the two flasks and the funnel with 50 cc. of hot distilled water, bringing the total solution in the flask to 400 cc. From the moment when the solution starts boiling, continue the boiling under constant stirring for exactly 15 min., when the stirring should be interrupted and the flask removed. Rinse the condenser, as well as stirrer, with hot water into the flask.

Pour the contents of the flask onto a Büchner funnel (7 cm.) with double filter paper (S & S 595 has proved very satisfactory) and filter rapidly under suction without allowing the material on the filter to become dry. Then wash with hot distilled water until the filtrate contains no more copper (potassium ferrocyanide test).

Empty the contents of the funnel, including filter paper, into a porcelain dish, rinse the funnel carefully with 6.5 per cent nitric acid, and heat the dish on a water bath until the precipitate is dissolved. Filter the solution off in the Büchner funnel through filter paper and treat the fibrous mass, either on the filter or after removing to the porcelain dish, with a concentrated ammonia solution, which should then be added to the first filtrate. By washing with 6.5 per cent nitric acid solution and afterwards with hot distilled water, all copper precipitate is removed. (Test with potassium ferrocyanide.)

Evaporate the acid filtrate in a porcelain dish and determine the copper by electrolysis. Knowing the exact weight of copper and of bone-dry cotton fiber, the copper number can be expressed as the quantity of copper per 100 g. of bone-dry fiber.

DETERMINATION OF CELLULOSE NUMBER—Place about 3 g. air-dry cotton (accurately weighed) and 250 cc. cold distilled water in the round-bottom flask. To this add 100 cc. of cold Fehling solution and 50 cc. of cold distilled water and let the solution stand for 45 min. under frequent stirring. Collect the fibrous mass on a Büchner funnel with double filter and wash, first with about 1000 cc. of cold distilled water, and afterwards with hot water. Determine the copper precipitate as outlined above and express the cellulose number in copper per 100 g. bone-dry fiber. The cellulose number subtracted from the copper number as determined above gives the "corrected copper number."

DETERMINATION OF HYDROLYSIS NUMBER[4]—Place about 3 g. air-dry cotton with 250 cc. sulfuric acid solution of 5 per cent strength in the round-bottom flask, and heat the contents under continuous stirring to the point of boiling. Continue the boiling for exactly 15 min., at which time neutralize the contents with sodium hydroxide solution (10 g. in 25 cc. water), add 100 cc. hot Fehling solution and 50 cc. hot water as described under "Copper Number," and boil for 15 min., after which determine the copper as above.

The hydrolysis number is the amount of copper obtained with 100 g. bone-dry fiber. Corrected hydrolysis number is found by subtracting the cellulose number from this value. The hydrolysis difference is determined by subtracting the copper number from the hydrolysis number.

The determination of α-cellulose is being undertaken by Bjarne Johnsen of the Hammermill Paper Co., Erie, Pa.

HAROLD HIBBERT, *Chairman*
W. F. HENDERSON
BJARNE JOHNSEN
W. O. MITSCHERLING
L. E. WISE

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[4] Schwalbe and Sieber, "Betriebskontrolle in der Zellstoff- und Papierindustrie," **1922**, p. 243.

Questions and Answers

We have been called upon to obtain certain information regarding apparatus and supplies and give a few examples below for the information of chemists:

Q.—Are American manufacturers producing graduated glassware of a grade acceptable for certification by the Bureau of Standards?

A.—Approximately 90 per cent of the graduated ware received for certification is American-made, and dealers who stock certified ware report that even a larger percentage of their stock has been made in this country.

Q.—Can 1000-cc. bottles of American manufacture be obtained?

A.—Such bottles are obtainable, though not ordinarily listed according to the metric system, for the reason that they are made from commercial molds. The best of these purchased from reliable dealers are excellent in quality, though not the cheapest, and hold the capacities indicated in the lists. At least one dealer has developed a batch glass formula of a resistant glass from which he has these bottles made.

Q.—Can rubber stoppers, satisfactory for combustion and other work, be obtained? Are they as good as those which we formerly imported?

A.—Rubber stoppers of all grades are stocked by the trade, but unfortunately most of them are purchased by the consumer on a cost basis. Not only rubber stoppers, but other rubber goods of a quality equal to the best obtainable anywhere may be had in this country, but they must be purchased on a quality basis, preferably after the examination of samples. As a rule such goods cost from 30 to 50 per cent more than those ordinarily offered by the trade, although the appearance and the specific gravity may be the same.

One dealer writes us: "A still better stopper than ours can be made either in the United States or abroad, and we shall be glad to reëstablish such a stopper if there is evidence of a reasonable demand. We have had no such evidence in our own recent experience."

Q.—What about glass tubing?

A.—Pyrex of heavy wall seems to be customarily used for organic combustions. There is satisfactory tubing available for glass blowing, and while a year or two ago there was some unsatisfactory material on the market, this has largely disappeared and the makers generally are anxious to satisfy the demand as to quality, size, etc.

Q.—What is the present status of American-made reagent chemicals? Sometimes chemicals are received which bear inordinate amounts of substances which it would seem ordinary care should eliminate in the process of manufacture. We appreciate what a few manufacturers are endeavoring to do, but it does seem that reagent chemicals, which lie at the basis of all our work, remain the weakest point in the American line of scientific products. What is the answer?

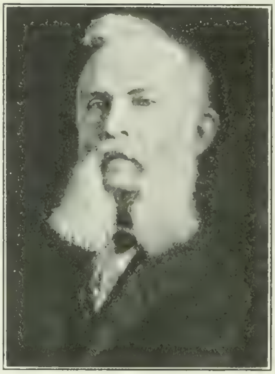
A.—Among some dealers there is the belief that the principal difficulty lies in the desire of the buyer to regard price only. However, the A. C. S. Committee on Guaranteed Reagents and Standard Apparatus will endeavor to obtain the answer to this question in a symposium planned for the Milwaukee meeting. The experience and recommendations of manufacturers, dealers, and users are wanted. Those willing to contribute to the discussion are invited to send detailed information to W. D. Collins, U. S. Geological Survey, Washington, D. C., as early as convenient.

May we assist in answering your questions?

AMERICAN CONTEMPORARIES

William Francis Hillebrand

If heredity and environment make us what we are, their influence can be seen in Dr. Hillebrand. His grandmother was an observant and lively old lady, if one can judge from certain passages in her diary, and his father was not only a physician, but a botanist whose garden is still one of the show places in Honolulu. Dr. Hillebrand was born in Honolulu, December 12, 1853. His boyhood was spent in the Sandwich Islands and California, he visited Japan, and the last two years of his teens were passed in Ithaca as a student at Cornell. It is not surprising that he is not only a scientist, but also a nature lover, interested in plants and birds, and fond of gardening. It is harder to say why he was for many years much interested in philately.


Harris & Ewing

W. F. Hillebrand

He is fond of music and his favorite game of cards is skat. He rises to the spirit of a social gathering with good grace. He has graduated from the ranks of baseball fans, but so recently that those who sit at lunch with him every day still indulge in mild banter at his expense. Though an enthusiastic angler for small-mouthed bass, Dr. Hillebrand will not be enticed by the salt-water fishing of the Chesapeake and the lower Potomac. Who shall say whether his patience at fishing makes him more careful and particular about the details of laboratory work or the reverse?

At the end of his sophomore year at Cornell, Dr. Hillebrand began his studies in Germany, at first under Bunsen. In 1875, with T. H. Norton, he was the first to prepare metallic cerium, lanthanum, and what was then called "didymium." His determination of the specific heats of these metals showed for the first time that they are trivalent, and therefore not members of the calcium family as had been supposed. He discovered that cerium gives off sparks when filed. Decades later this behavior came to be of commercial value for gas lighters.

Another discovery of far greater economic importance is recalled here. In 1904, Dr. Hillebrand called attention to the possibility of recovering and utilizing the enormous quantities of potash that are volatilized during the clinkering of portland cement. He is too seldom given credit for suggesting what is now an accomplished fact.[1]

After leaving Heidelberg, Dr. Hillebrand studied for a time under Fittig at Strassburg. This was his only digression into organic chemistry, but even then one of the two papers he wrote at that time was a crystallographic study. He returned to his proper field when he went to the Mining Academy at Freiberg, and has never since left it. For a while he worked as an assayer at Leadville in its roaring days. Then followed a period of five years, 1880 to 1885, at Denver with the Geological Survey, after which he was transferred to Washington, where he still lives.

The outstanding feature of Dr. Hillebrand's work has always been his placing of mineral and rock analysis upon the high plane of the utmost attainable accuracy. Not for him the easy expedient of making analyses sum up exactly 100 per cent by putting in just the right amount of "undetermined." His "traces" are not small determinable quantities, but real traces Many of his determinations of small fractions of a per cent of the less abundant constituents of rocks have been of illuminating value to the geologist by bringing to light unexpected differences or similarities.

Honesty in analytical work cannot but have its influence upon the daily life and contacts of him who practices it. Dr. Hillebrand once said that he was selected as chief chemist of the Bureau of Standards because of his reputation as an analyst. Perhaps it has never occurred to him that unwavering integrity in all his dealings may have had more to do with his selection than he suspects.

"For great examples justify command."

Dr. Hillebrand's attention to apparently trifling details is well illustrated by his account of the discovery of the gas which years later he called to the attention of Ramsay, who showed it to be helium. In 1890 he observed the slow and long-continued evolution of tiny bubbles from a sample of uraninite that had been treated with hydrochloric acid in a test tube. He found that the gas was neither carbon dioxide nor hydrogen sulfide, and he is not to be blamed for thinking that it was nitrogen.

Nothing better shows Dr. Hillebrand's self-effacement than this placing of a possibly great discovery in Ramsay's hands.

When his work came to be known by other chemists, Dr. Hillebrand was constrained to write the first of a series of five bulletins of the Geological Survey, in which his analytical methods are described. The first two, Nos. 148 and 176, take into account only the silicates. The others, Nos. 305, 422, and 700, deal also with the carbonate rocks. Each is a revision and enlargement of its predecessor. German translations of three of them have been published.

Dr. Hillebrand has not the teacher's temperament, but is essentially a laboratory man. His preëminence rests upon that. Because of it he was president of the American Chemical Society in 1906, and became a member of the National Academy of Sciences in 1908. For a long time he was on the editorial boards of our two journals, and for many years he has been chairman of the Supervisory Committee on Standard Methods of Analysis.

Few members of the Society know that most of the credit for the establishment of This Journal belongs to Dr. Hillebrand. Early in 1906, when he was president, he was told of the danger of a split in the Society because many of the members felt that industrial chemistry was being slighted in what was then our only journal. To make a long story short, prompt action was taken, there was much correspondence, and many consultations were held to decide whether it was advisable to start a new journal, how it could be financed, what its policies should be, and whom to select as editor. All these matters were finally settled and the first number of This Journal was issued in January, 1909.

Dr. Hillebrand's passion for exactness and precision is not confined to laboratory work. He is equally insistent upon the use of precise, clear, and grammatical English. It would be impossible to estimate the value of his editorial criticisms of papers submitted for publication in our journals or written by members of the staff of the Bureau of Standards. He will not tolerate an official letter carelessly written by one of his subordinates. In this he is not arbitrarily annoying, but is willing to debate with the culprit about the choice of a word or phrase, or about the tone of a whole letter. He has not forgotten his own early papers that were returned for revision after a liberal blue-penciling by Dr. Remsen, whose suggestions, he admits, always improved the papers. Dr. Hillebrand's contributions to *Chemical Abstracts* were always among the most carefully prepared.

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[1] *Proc. Am. Soc. Testing Materials*, **4** (1904), 465.

This is the man who has led the Chemistry Division of the Bureau of Standards since 1908, and under whom its work has become important in many fields; who has under him a body of chemists who respect and admire and are loyal to him. To these he is "The Doctor," a title less austere and distant than "The Supreme Court," as he used to be called by the chemists of another bureau, who did not have daily contact with him.

C. E. WATERS

SCIENTIFIC SOCIETIES

American Leather Chemists Association

The twentieth annual convention of the American Leather Chemists Association, held at the Greenbrier, White Sulphur Springs, W. Va., June 7 to 9, was enjoyed by a large and enthusiastic number of members and friends.

Research was the keynote of the meeting. Fraser M. Moffat, president of the Tanners' Council, which recently appropriated $110,000 for the establishment of a Tanning Research Institute at the University of Cincinnati, gave an inspiring address on the problems and needs of the tanning industry, and pointed out the necessity of proving to the public the truth of the tanners' slogan, "Nothing takes the place of leather." He was followed by Harrison E. Howe, editor of *Industrial and Engineering Chemistry*, who spoke on "Research an Industrial Investment."

Addresses were made by well-known colloid chemists. Martin H. Fischer, of the University of Cincinnati, spoke on "Some Scientific and Technical Aspects of Emulsion Chemistry;" Jerome Alexander spoke on "Degree of Dispersion as an Influence in Tanning." G. D. McLaughlin, director of the Research Laboratory of the Tanners' Council, and his assistants, E. R. Theis and E. Rockwell, presented papers giving the results of some of their research work on the "Science of Soaking and the Bacteriology of Curing Animal Skin."

An interesting contribution was a paper from the Proctor Research Laboratory, Leeds, England, by J. R. Browne, F. C. Thompson, and W. R. Atkin, on "The Ultrafiltration of Tannin Solutions with Special Reference to Tannin Analysis;" Allen Rogers, of Pratt Institute, Brooklyn, gave an interesting talk on leathers of marine origin, and exhibited a reel of films showing the capture of various kinds of sharks, porpoises, andrays, which, considering the fact that tanners use also the skins of cattle, horse, alligator, snake, lizard, etc., shows that the tanner "has all nature skinned" in his effort to serve the public.

Committee reports on a wide variety of topics were presented by G. W. Schultz, R. W. Frey, Lloyd Balderston, Thomas Blackadder, and H. C. Reed. The reports were the basis of a lively discussion by the members, as were also the following papers: "Determination of Free Sulfuric Acid in Vegetable Tanned Leather," by R. W. Frey, S. Kohn, and T. J. Mosser; "Elucidation of Details of Method for Determination of Free Sulfuric Acid in Vegetable Tanned Leather," by J. S. Rogers; "Extraction of Oils, Fats, and Waxes from Leather," by Lloyd Balderston; "Effects of Sodium Chloride, Sodium Sulfate, and Sodium Acetate on Precipitation Figure and Tanning Properties of a Chrome Liquor," by Donald Burton; "Further Observations on the Histology of Bated Skin," by C. S. Hollander; "Study of Some of the Processes Involved in Tannin Analysis," by G. W. Schultz; and "Direct Measurement of Plumping Power of Tan Liquor," by R. W. Hart.

The following officers were elected for the next year:

President: C. C. SMOOT, III, North Wilkesboro, N. C.
Vice President: J. S. ROGERS, Morgantown, N. C.
Secretary-Treasurer: H. C. REED, 22 East 16th St., New York City
Councilors: J. E. BREITHAUPT, Kitchener, Ont.; R. W. GRIFFITH, Canton, N. C.; G. D. MCLAUGHLIN, Cincinnati, Ohio; C. R. OBERFELL, Lynchburg, Va.

Chemical Exposition Plans Buying Fair

At a meeting of the Advisory Committee of the Ninth National Exposition of Chemical Industries, held June 6 at the Chemists' Club, New York, the plan to make the exposition which will be held this year at the Grand Central Palace, New York, during the week of September 17 to 22, a huge chemical "buying fair," was placed before the committee. The plan as outlined suggested that each exhibitor make every effort to display his goods in a novel method and in a manner which, to some degree at least, will demonstrate their particular characteristics, special uses, and selling points. It was also suggested that all exhibitors arrange to have as nearly as possible their full sales forces at the exposition, so that they might not only attend company sales conferences in conjunction with the exposition, but also attend joint sales conferences composed of the sales staffs of all the exhibitors. With the large number of chemical and chemical equipment consumers who attend the exposition each year, this sales contact on a large scale, away from the offices of the buyers, was pointed out as very desirable.

A tentative report from H. S. Kimberly, of Washington, who has been selected by the committee to arrange the educational exhibits at this year's exposition, was heard. The chief object of the exhibits will be to demonstrate to the business man just what chemicals can do and are doing, and the place of chemistry in business. The Chemical Warfare Service and the Bureau of Chemistry of the Department of Agriculture will have two large displays among the educational exhibits. Chemicals of the kitchen and the chemistry of food are also included. The results of research on a scientifically correct antiknock and carbon compound for internal-combustion engines will be demonstrated.

Calendar of Meetings

American Chemical Society—66th Meeting, Milwaukee, Wis., September 10 to 15, 1923.

9th National Exposition of Chemical Industries—Grand Central Palace, New York City, September 17 to 22, 1923.

American Electrochemical Society—Fall Meeting, Dayton, Ohio, September 27 to 29, 1923.

Cereal Chemists Meet in Chicago

The first convention of the American Association of Cereal Chemists held since that association amalgamated with the American Society of Milling and Baking Technology, was convened in Chicago during the week of June 3, 1923. With S. J. Lawellin presiding, the program was opened Tuesday morning at the Hotel Sherman, with a paper by C. H. Briggs, entitled, "Has Northwestern Spring Wheat Deteriorated?" C. E. Mangels presented "Recent Investigations on Durum Wheat Conducted at the North Dakota Experiment Station;" C. H. Bailey talked on "The Use of the Viscometer in Flour Strength Studies," and Washington Platt on "The Action of Shortenings."

The Wednesday sessions were devoted to association business. M. J. Blish, chemist of the Nebraska Agricultural Experiment Station, was elected president of the association. Other officers elected were: R. B. Potts, vice president; R. K. Durham, secretary-treasurer; J. R. Hess, managing editor; C. H. Bailey, editor-in-chief. Progress was made in the direction of revising the constitution.

The Thursday sessions were held at the American Institute of Baking. Members of the Institute staff contributed to the program, which included papers by A. W. Landstrom, on "Homogenization Applied to Baking;" L. A. Rumsey, on "Some Aspects of Enzyme Action in Flour Strength and Fermentation Control;" A. W. Hall, on "Building the Quality Loaf;" and C. B. Morrison, on "Bread *vs.* Vitamins." Other papers presented included "Moisture Determinations," by H. G. Nelson, and "Protein Content *vs.* Texture *vs.* Kernel Weight in Southwestern Market Run, Hard Winter Wheat," by W. L. Frank. Practical demonstrations and baking experiments were conducted in the shops and laboratories of the American Institute of Baking.

Friday forenoon the presentation of papers was continued at Hotel Sherman. These included "Self-Rising Flour," by L. H. Bailey; "Chemical and Physical Changes of Some Constituents of Flour as Affected by Bleaching," by J. C. Baker; "Relation of Bakery and Mill Laboratories," by Rowland J. Clark; and "A Suggested Control for Checking Nitrogen and Protein as Determined by the Kjeldahl Method," by S. J. Lawellin. A luncheon was served at the City Club after the morning session. During the afternoon a business session disposed of the remaining convention business.

The cereal chemists were afforded an opportunity to mingle with the flour-millers, since the Association of Operative Millers held its annual convention in the same hotel during the week of June 3. Representatives of the Association of Cereal Chemists appeared by invitation before the convention of millers for the discussion of chemical subjects of mutual interest.

Plans for the further development of the association's journal were discussed at some length, and a decision reached to expand this publication somewhat during the next calendar year. It appears probable that at least six issues will be printed in 1924, possibly under a new and distinctive name. Plans will be formulated and announced by the editorial board at a later date.

First National Symposium on Colloid Chemistry

The First National Symposium on Colloid Chemistry, meeting in Madison from June 12 to 15, on invitation of the University of Wisconsin, was an unqualified success. It exceeded even the expectations of those directly responsible for its inception. The forty-minute period allowed each speaker for the presentation of his paper, the thoroughness of the discussions following each presentation, and the opportunity afforded for closer association between visitors, furnished another argument for the supporters of the opinion that there might well be substituted for at least one of the meetings of the AMERICAN CHEMICAL SOCIETY, a group of intersectional meetings.

The symposium assumed somewhat an international aspect in that, besides the honor guest, Prof. The Svedberg, of the University of Upsala, Sweden, there were present representatives of Canadian universities, while the roster of visitors included at least one from Pretoria, South Africa, and several from China. Approximately 200 visitors from one-half of the states in the Union were present, and of these one-fourth were from the industries, about 28 of which sent members of their staffs of executives and technical men.

A wide diversity of subjects was discussed by experts in their respective fields, including the presentation of theories of emulsification and lyophillic colloids, the formation of organic and inorganic jellies, problems of protein behavior, of adsorption, of dialysis, and of emulsification, the practical application of colloid chemistry to problems of food production and practical photography, and to the manufacture of lubricants, adhesives, rubber, leather, enzymic, and animal glandular products.

The success of the symposium has prompted the Colloid Committee of the National Research Council to vote to make it an annual affair. The next meeting place is to be at Northwestern University, in June, 1924.

H. A. SCHUETTE

MADISON, WIS.

NOTES AND CORRESPONDENCE

The Resilient Energy and Abrasion Resistance of Vulcanized Rubber

Editor of Industrial and Engineering Chemistry:

Referring to the paper on "The Resilient Energy and Abrasion Resistance of Vulcanized Rubber," by H. W. Greider, published in THIS JOURNAL, **15** (1923), 504, I beg to submit a few remarks, especially since the entire field of investigating the wear resistance of all our materials used under certain kinds of friction—metals, building materials, textiles, rubber, etc.—has been sadly neglected in this country, although the property of resistance to abrasion is in a great many cases of far greater practical importance than strength, hardness, and other properties usually covered by routine tests.

First of all, abrasion tests of materials are of practical value only if they are undertaken in such manner that the particular form of friction which the material has to bear in practice is exactly reproduced. There are great differences, for instance, in the kind of friction encountered in a ball or roller bearing, in a locomotive wheel against the rails, and in a shovel or plow blade. Running metal or rubber against an arbitrarily selected abrasive material is in most cases no duplication of service conditions, and the value of such tests for the classification of materials is questionable. I believe that Fig. 11 in the paper shows clearly that something else is "going on" with the surface of a tire than what has been done to the rubber specimens in the laboratory investigation. In other words, the stresses encountered in practice are of a different nature.

It is regrettable that the author does not give any information on the method he used to measure the "resilient energy" of rubber compounds.

On page 508 the author states: "It has long been recognized that in metals, concrete, stone, and other engineering materials, resistance to abrasive wear is intimately associated with the hardness of the material, and it is not clear why hardness has not previously received more consideration as a factor in the toughness of rubber."

As far as metals are concerned, all investigators—such as Robin, Nusbaumer, Stanton, Saniter, Brinell—have found that *no* relation exists between "hardness" and resistance to abrasion. One of the most careful investigations ever carried out on this important subject was undertaken by the Institution of Mechanical Engineers, London, and the results were published in the 1916 "Report of the Hardness Tests Research Committee" of this institution.

Some of the difficulties encountered in all researches of this kind are at present unsurmountable. "Hardness" of metals is usually defined as "resistance to *permanent* deformation," but no means have yet been found to determine this resistance. What we are doing is to investigate the resistance of progressively deformed metals to gradually increased deformation, taking an entirely arbitrary end-point. If we would apply our metal-hardness testers (Brinell or scleroscope) to hardness tests of vulcanized rubber, we would find that rubber is harder than iron. Hardness of rubber is something entirely different from hardness of metals, and I do not believe that hardness of rubber has ever been determined; this depends, of course, on how we decide to define "rubber hardness." Instruments like a durometer or plastometer compare properties of elastic compressibility by means of arbitrarily shaped and dimensioned tools, which, however, do not produce a permanent indentation or penetration of the rubber. These tests are carried out *below* the elastic limit of the material, and are therefore of a nature entirely different from that of the usual mechanical hardness tests of metals.

Mr. Greider's paper is of great interest, and his results are undoubtedly of considerable value to the industry, but he uses his terms of mechanical properties—such as resilient energy, resilience, toughness, hardness, etc.—in a manner which would tend to indicate that he is speaking of "standard" units and recognized values of properties of the material, which—as everybody must regret—is by no means the case. Unfortunately, we do not yet know anything regarding resilient energy, toughness, or hardness of rubber.

HERMAN A. HOLZ

17 MADISON AVE
NEW YORK, N. Y.
May 7, 1923

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Editor of Industrial and Engineering Chemistry:

The principal point at issue, as I interpret the comments of Mr. Holz, is my use of the term "hardness" with reference to a physical property of vulcanized rubber. I am quite aware that "hardness" of rubber is not identical with "hardness" of metals. I have used the term in the sense recognized by every rubber technologist, as measured by instrument in common use in the rubber industry to determine this property. For a further description of these instruments (durometer, densimeter, and plastometer) and a study of their measurements and of the nature of "hardness" in vulcanized rubber, I must refer Mr. Holz to the paper by Gurney, on "The Modulus of Hardness of Vulcanized Rubber" [THIS JOURNAL, **13** (1921), 707].

While I have not attempted to define "hardness" in my paper, I have shown that, at least with respect to the influence of added pigments, the property measured by the durometer, and termed hardness, is substantially identical with the *rigidity* (stiffness) of the rubber, as determined by the stress load required to produce 300 per cent elongation (compare Figs. 8 and 9 in my paper). Wherever I have used the word "hardness" in the paper I have usually included in parentheses, as synonymous, the word "rigidity."

I have no desire to appear controversial with respect to the physical properties of metals, of which I claim no special knowledge. Nevertheless, it should be permissible to point out that, even in the case of metals, the property of "hardness" lacks exact definition. Upon this definition hinges the assertion of Mr. Holz that numerous investigators have found *no relation* between hardness and abrasion resistance in metals. As ordinarily used with reference to metals, the term "hardness" embodies several concepts: scratch hardness (the Moh scale and its modifications), indentation hardness (Brinell), elastic impact or rebounding hardness (Shore scleroscope), cutting hardness (micro-sclerometer), tensile hardness or resistance to permanent deformation. The Brinell hardness number measures the resistance of the metal to *plastic deformation.* In writing this paper, I had in mind a possible analogy between the abrasion resistance of rubber and that of bearing alloys.

I would call Mr. Holz's attention to a recent paper by Bierbaum in *Chemical and Metallurgical Engineering,* **28** (1923), 304, in which he uses the term "hardness" as practically synonymous with cutting or abrasion resistance, and devises a "micro-cut" method of determining the hardness of metals used in bearing alloys.

Mr. Holz's remark that the durometer and plastometer measure "elastic compressibility" signifies nothing to a rubber physicist. Rubber is substantially incompressible, but it is readily deformable. The stress-strain curve of rubber may be determined either in compression or tension, but what these instruments really measure seems to be the property of rigidity, a characteristic of all solid substances. To say, therefore, that rubber has greater "hardness" (rigidity) than iron, cannot correctly characterize the material. Rubber probably has no elastic limit except its rupture strength; it does not follow Hooke's law, and every stress, however slight, produces some permanent deformation, and it is, therefore, quite impossible to measure "hardness" *above the elastic limit of the material.*

The "resilient energy" capacity, regarding the measurement of which Mr. Holz asks to be informed, was determined by the previously published methods of Wiegand [*Can. Chem. J.*, **4** (1920), 160] and of Gurney and Tavener [THIS JOURNAL, **14** (1922), 134], a planimetric determination of the area between the stress-strain (tensile) curve and the elongation axis. The energy capacity may also be determined from compression stress-strain curves. I have not attempted to define "toughness" of rubber further than to say that it is usually considered to be an optimum combination of tensile strength, abrasion resistance, endurance of flexing, resilience, and relatively low permanent set. Resilience may be defined as the ability of the material to return to its original conformation and dimensions following the application of a deforming stress, and in rubber it has at least two elements—high rate of return and absence of great permanent deformation (permanent set). While these quantities are perhaps not as yet accepted "standard" units, they are, at any rate, generally recognized by rubber technologists.

I shall not undertake to defend laboratory tests of abrasion resistance; their value is already sufficiently appreciated in the rubber industry. Mr. Holz is correct in saying that laboratory abrasion tests do not exactly duplicate road conditions, but it is neither necessary nor desirable that they should. I am heartily in accord with his emphasis on the desirability of further investigations in the field of abrasion resistance, but find myself unable to agree with the claim that "we do not yet know anything regarding the resilient energy, toughness, or hardness of rubber."

H. W. GREIDER

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
PITTSBURGH, PA.
May 14, 1923

TOKYO LETTER

By K. KASHIMA, 994 Ikebukuro, near Tokyo, Japan

ANNUAL MEETINGS

April is the month of cherry blossoms and general meetings. On the 1st and 2nd, the annual meeting of the Mathematical and Physical Society of Japan was held in Tokyo. On the 7th and 8th, the 45th annual meeting of the Chemical Society of Japan was held at the chemical laboratory of the Faculty of Science of the Tokyo Imperial University. The Sakurai Medal was awarded to Shintaro Kodama for which the medalist read a paper on amino acids and aldehydes. Professor Katayama gave the presidential address, on stoichiometry. The general meeting of the Pharmaceutical Society of Japan was held at the City of Tokushima on the 14th and 15th of April. The 26th annual meeting of the Society of Chemical Industry was held in Tokyo on the 5th and 6th of May. Shuichiro Nagai, of the Faculty of Applied Chemistry of the Tokyo Imperial University, was awarded with the society's medal for the work on safrol from camphor oils. K. Saegi gave the presidential address.

SYNTHESIS OF PETROLEUM

Petroleum in this country is not abundant. For some time chemists have been conducting experiments to investigate the origin of petroleum.

Kiuhei Kobayashi, of Waseda University, has made studies on Japanese acid clay (fuller's earth), and has published a book, "Acid Clay," which is the only book on this subject. On distilling a mixture of sodium chloride and the clay, he obtained hydrochloric acid. This curious fact led him to seek further facts. Fish oil was then used instead of salt. He distilled a mixture of the oil and the clay, covered with the same amount of the clay. A petroleum-like oil having greenish fluorescence was distilled over. After washing with sulfuric acid, caustic soda solution, and water, as in the petroleum industry, the insoluble oil was fractionally distilled into gasoline (about 30 per cent), lamp oil (50 per cent), and middle oil (10 per cent). He claims that the petroleum which he has prepared from fish oil has physical properties which are almost identical with those obtained from the natural petroleum, the yields being about 60 per cent of the oil. The product is mainly composed of naphthenic hydrocarbons containing a comparatively large amount of olefinic hydrocarbons. Based on these results, he proposes an hypothesis on the cause of formation of natural petroleum.

Other chemists have also engaged in this work and many papers have been published in *Chemical Industry* (*Japan*), *The Journal of the Chemical Society of Japan*, and the *Patent Journal;* readers will be able to get their outlines through *Chemical Abstracts*. As material, fish oils of different origin—vegetable oils, calcium salts of fatty acids from soy bean, pine resin, sodium salts of fatty acids from herring oil, pupa oil, etc., were used. Acid clay is a curious substance; when a mixture of the clay and camphor is heated, petroleum is formed.

Not only are fish oils used for the manufacture of petroleum, but also calcium or sodium salts of fatty acids. When treated with lime, glycerol is produced from the oil, the yield of this material being about 10 per cent. This reduces the price of the oil by 13 to 45 per cent and also that of the petroleum. The process has now passed the period of laboratory experiment. When the writer had a chance to journey through Echigo for inspection of the petroleum industry two years ago, one company was manufacturing petroleum from fish oil in apparatus with a capacity about 10 koku (1 koku = 180.39 liters).

The annual production of fish oils in this country is not clearly recorded, but it is estimated to be about 3,000,000 kan (1 kan = 3.75 kg.). Some of this is used for lubricating oils, etc., but a large part may be used for the manufacture of petroleum.

J. Takahashi in his book, "A New Treatise on the Mineral Deposit of Petroleum," reports a comprehensive and complete investigation of the mineral deposit in the petroleum fields of Japan.

GASOLINE FROM NATURAL GAS

This subject is an internationally popular one. The drying material of Dr. Ikeda, mentioned in a previous letter and now called "adsole," has proved to be a powerful drying agent and is now being used in many industries. Fish are easily dried by this material. It has also been found that adsole will absorb gasoline from natural gas, from which the gasoline is recovered. The Tôyô Gas Laboratory has been founded for the utilization of adsole, manufacture of gasoline and other connected works, being connected with the Rikwagaku Kenkyujo (Institute of Physical and Chemical Research). A plant was built in Echigo, a famous petroleum field in Japan, and the work is now progressing. In the future some report will be written on the work of this plant.

May 26, 1923

WASHINGTON NOTES

Encyclopedia of Specifications

On May 26, 1923, Secretary Hoover called a conference of state purchasing agents at the Department of Commerce, upon specifications for the purchase of supplies by our national and local governments and public institutions. Twenty-six state governments were represented at this conference. Secretary Hoover announced that the work contemplated is an important link in the whole great chain of elimination in our industrial and commercial fabric, and means hundreds of millions of dollars to the taxpayer and much more to the private consumer and to the manufacturer.

He learned from war experience of the great faultiness of specifications used in federal purchases and soon after becoming Secretary of Commerce determined that his department should review these specifications. Subsequently, an interdepartmental committee was created for the better development of this work under the leadership of the Department of Commerce. Each of the specifications is being considered and the chemical and physical requirements of each article are being exhaustively examined in the laboratories of the Bureau of Standards. After a definite scientific background has been determined, the manufacturers in each branch are consulted to make sure that the industrial and commercial setting of a specification is right from the point of view of the practical producer.

These reorganized specifications have enabled the Government to buy on so much better terms that Secretary Hoover called the conference of purchasing agents with the thought that the Federal Government—with its great laboratories and with its large experience in the standardization of purchases, in the formulation of the sequent specifications, and in the development of methods of testing—could be of inestimable service to the purchasing agents of states, municipalities, and public institutions.

Where standards and specifications are successfully developed by the Government, they are receiving wide voluntary acceptance and adoption among public consumers, and many industries are now applying to the Department of Commerce to establish standards upon which specifications may be founded. The simplification of dimensions in many common articles is also a branch of standardization.

The direct purpose of this coöperative work is to secure among federal, state, and municipal groups constructive application of scientific knowledge to service requirements; to coördinate similar demands and eliminate unessential differences; to balance increases in cost against probable service improvements; and to formulate adequate test or inspection methods. A handbook will be formulated and issued for the use of public purchasing agents, covering the entire field of standards, specifications, simplifications, and tests which may be determined as the best adapted for public purchases, the publication in each instance to be formulated in consultation with the different agencies particularly concerned.

The work in the Department of Commerce will be in charge of A. S. McAllister. Dr. McAllister has for some time been liason officer between the Department of Commerce and the American Engineering Standards Committee, with headquarters in New York, N. Y., but at the request of Secretary Hoover he has been released by the American Engineering Standards Committee and transferred to Washington to head this work.

A further conference was called on June 11 at the Department of Commerce for the formulation of an advisory committee to coöperate with the Department of Commerce and the State Purchasing Agents' Association in this work.

The associations represented at this conference were:

American Engineering Standards Committee
American Society for Testing Materials
National Association of Purchasing Agents
United States Chamber of Commerce
National Association of Manufacturers
American Hotel Association
National Business Editors' Association
Federal Specifications Bureau
Associates for Government Service
American Electric Railway Association
Society of Automotive Engineers

Nitrate Survey

In connection with the nitrate investigations being conducted by the Department of Commerce, it is understood that Frank A. Ernst will shortly visit Europe, accompanied by J. M. Braham of the Fixed Nitrogen Laboratory. J. Foster Bain, director of the Bureau of Mines, and H. S. Mulliken, his technical assistant, will go to Chile to investigate conditions there. Arthur H. Walker, vice president of the American Farm Bureau Federation, is traveling about the United States, visiting in particular the agricultural experiment stations and agricultural colleges, with a view to securing information on the needs of agriculture for nitrates and the prospect of increased payments for this purpose. He is being assisted by R. F. Bower, who is at present stationed in Washington. R. S. McBride has been appointed special agent to report upon nitrogen from coal.

Dye Census

The manuscript on the "Census of Dyes and Other Organic Synthetic Chemicals," prepared by W. N. Watson of the Tariff Commission, is now in the printer's hands, and it is hoped that the printed report will be available for distribution soon after the middle of July. The principal feature of the report this year is the discussion of the international dye trade, with complete figures on exports and imports of all the dye-consuming nations of the world. The work on non-coal-tar products, which appeared last year for the first time, is continued.

Dye Committee Meets

C. G. Derick, Wm. J. Hale, W. H. Watkins, L. A. Olney, and R. N. Shreve, the committee of collaborators recently appointed to the Color Laboratory of the Bureau of Chemistry, Department of Agriculture, visited Washington on June 11 and 12. After a conference with W. G. Campbell, acting chief of the Bureau of Chemistry, and W. W. Skinner, assistant chief, they inspected the Color Laboratory, which is situated at the Arlington Experimental Farm, Va., and discussed the present and future work of the laboratory with J. A. Ambler, chemist in charge. The committee also visited the Bureau of Standards, Department of Commerce, conferred with G. K. Burgess, director, and inspected the work on dyes which is being carried on by that bureau.

This committee was appointed some time ago by the Section of Dye Chemistry of the American Chemical Society to coöperate with those government laboratories which are working on dyes and to suggest to them problems of vital interest to the dye industry.

New Industrial Film

"The Story of the Gasoline Motor" is the title of the latest issue in the series of industrial motion picture films prepared by the Bureau of Mines. This film, made in coöperation with the Continental Motors Corporation, visualizes in a most graphic manner the complete operation of a gasoline engine. Special views have been made to show the cycles through which the gas travels from the time it enters the engine as an explosive mixture until the time it leaves the engine as a burned gas. With the aid of special lenses, some unusual "close-up" scenes have been obtained. In order to show clearly what has taken place inside the engine and the particular role which each part plays in creating power from liquid fuel, much elaborate work was done. To give this correct portrayal in every detail, many engines were cut into at various points and made to operate so the particular function of every moving part would be clearly shown. Copies of this film may be borrowed for educational purposes from the Department of the Interior, Bureau of Mines, Pittsburgh, Pa.

Hydrogen Sulfide as an Industrial Poison

An investigation of the toxicity of hydrogen sulfide has been completed by the Bureau of Mines. The experiments show that this gas is exceedingly poisonous, as acute poisoning can be caused by breathing air containing as little as 0.07 of one per cent. Dangers from its possible presence in mines and around industrial plants have not been fully appreciated. The gas is frequently present in small but dangerous quantities in places where sulfur may be present and exposed to chemical action, as in mines, sewers, sulfuric acid plants, refineries, gas plants, and smelters.

June 20, 1923

CANADIAN LETTER

By S. J. Cook, 140 Broadway Ave., Ottawa, Canada

Production of Chemicals during 1922

Statistics recently issued indicate that the production of chemicals and allied products in Canada during 1922 reached a total value of $99,575,000 as compared with $87,185,102 in the preceding year.

Imports statistics reflected improved conditions in international trade, and the exports of Canadian chemicals and allied products showed a marked advance over the preceding year. Production records in almost every industrial field during the past three years showed the effect of post-war influences. In 1919, as a result of the large-scale production during the war years, the accumulation of stocks was considerably in excess of current requirements, with the result that production was much curtailed. Most of these stocks were disposed of in 1919, with the result that in the early part of 1920 an appreciable advance in prices occurred, which reached a maximum about the middle of the year. This advance in prices was followed by increased production, and in many industries 1920 was a banner year. During the closing months, however, demands from consumers for lower prices became more insistent, and in 1921 a nation-wide reduction of inventories and deflation in prices occurred. At the close of that year, although prices were at a much lower level than at the beginning, conditions throughout the industry were much improved and the prospects for conservative and consistent progress were much better than at any time since the close of the war. Substantial progress was made in 1922, and 1923 opened with conditions distinctly favorable for a marked advance in production reports.

In certain well-defined fields, the production of chemicals in Canada has attained world-trade importance. In many other lines, production in competition with imported chemicals is being carried on successfully, and the manufacture of specific commodities for which there is a definite and continuous demand has proved an attractive field for small concerns. Several plants have been established, each of which specializes in the production of one or more of these necessities for the chemical trade. A study of the imports statistics shows that many such opportunities exist.

The distillation of tar in Canada has been carried on as a separate industry by several plants for a number of years, and as an adjunct to the production of composition roofing by several other concerns. The products include creosote oils, naphthalene, pitch, benzene, naphtha, toluene, and road tars. The manufacture of disinfectants composed principally of coal has also been undertaken with considerable success.

The manufacture of heavy chemicals in Canada has been carried on for a great many years. The production of mineral acids was one of the earliest chemical industries to be established, and it has always shown great stability and strength. During 1922 the products made by the firms under the grouping acids, alkalies, salts, and compressed gases, reached a total value of nearly $17,600,000, an increase of more than $4,000,000 over the value of the 1921 output. The production of sulfuric acid alone increased more than 20,000 tons, to a total of 67,280 tons valued at $1,390,000. Calcium carbide, calcium and sodium cyanides, and soda ash were produced in increasingly large quantities during the year.

The manufacture of compressed gases, including oxygen, acetylene, carbon dioxide, anhydrous ammonia and hydrogen, continued on about the same scale as in the two preceding years, the total production being valued at $2,000,000.

There was a considerable increase in the production of explosives during 1922, and the production of ammunition including safety cartridges, detonators, electric detonators, and primers, was well maintained.

In the manufacture of matches two new plants were put in operation during 1922, one by the Canadian Match Company, of Pembroke, where formerly splints only had been manufactured, and the other by The Match Company, at Berthierville.

The production of fertilizers in Canada was carried on by sixteen plants, and the value of the output in 1922 was estimated at $2,400,000, in addition to the production of such materials by the industries classified in other groups. Conditions in the fertilizer trade during the past few years have been rather difficult, and the value of the output has consequently declined. On the other hand, imported fertilizer materials, such as muriate and sulfate of potash and nitrate of soda, have become available in greater quantity and at a lower price. As a consequence of this considerable quantities have been imported.

The selling value of the products made in the medicinal and pharmaceutical preparations industry was slightly less than the value credited to the output of these concerns in 1921, but in general it may be said that the industry maintained its established position.

The manufacture of paints, pigments, and varnishes continued to be Canada's leading chemical industry, and in 1922 the output of the plants in this group was estimated to be worth $23,960,000, at which figure a gain of nearly $6,000,000 in output valuation was attained. The figures for 1922 did not come up to the values established for 1920, but they indicated that a very considerable advance had been made by the industry.

The manufacture of soaps, washing compounds, and toilet preparations contributed products valued at $15,570,000, and at this figure the group ranked third among the chemical industries. Canada still imports more than $1,000,000 worth of soaps annually, mostly from the United States, nearly all of which comes under the headings "common laundry soap" and "toilet soap." On the other hand, the exports of Canadian soap go principally to the United Kingdom. The total value of the export trade is in the neighborhood of $200,000. The manufacture of washing compounds in Canada is one of the industries in which decided progress has been made. Three new plants were established in 1921. The ease of manufacture and the ready market for these useful preparations probably account for the increased prosperity.

While considerable quantities of perfumes, cosmetics, and toilet preparations are made as minor products of several other industries, the manufacture of these commodities as principal products has been carried on in Canada for a number of years, and the industry has become recognized as one of no mean importance.

The manufacture of printing inks continued to be the principal item of production in the inks, dyes, and colors group. The value of the group output in 1922, estimated at $2,200,000, was practically unchanged from the previous year.

The production of wood distillation products in 1922 continued on an even more modest scale than in the preceding year, which was one of the dullest in the history of the industry.

The manufacture of chemicals and allied products which do not naturally fall in any one of the groups previously considered, and including such commodities as adhesives, artificial abrasives, boiler compounds, flavoring extracts and jelly powders, polishes and dressings, sweeping compounds, baking powders, insecticides, and chemical products not elsewhere specified, was carried on by about one hundred and ten firms in Canada, and the value of their combined outputs in 1922 was estimated at $9,260,000, an increase of more than $1,000,000 over the totals for 1921.

The total importations of chemicals and allied products into Canada during the calendar year 1922 were valued at $25,689,000, an increase of $675,000 over the amount reported in the preceding year.

There was a very considerable increase in the quantities of sulfuric and hydrochloric acid imported into Canada during 1922, but the imports of nitric acid were slightly less. Oxalic acid importations were less, while the quantities of stearic, tannic, tartaric, and boric acids were greater than in 1921.

May 25, 1923

The Canadian Institute of Chemistry and the Canadian section of the Society of Chemical Industry held a joint meeting at the University of Toronto, May 29, 30, and 31. S. J. Cook, of the Dominion Bureau of Statistics, who was one of the principal speakers, gave statistics on the production, export, and import of chemicals and allied products in Canada.

Election of officers resulted as follows:

President: A. C. Neish, Queens University, Kingston

Vice Presidents: T. Thorwaldsen, University of Saskatchewan, Saskatoon; A. T. Charron, Provincial Chemist, Quebec; C. E. Wallin, Sydney, N. S.

Secretary: L. E. Westman, Toronto

Treasurer: J. Watson Bain, University of Toronto, Toronto.

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Prof. Georges Urbain has recently returned to France after a six months' visit to the United States, and he has given some very interesting impressions. He considers that American science will soon eclipse that in Europe. In the United States scientific research and higher instruction are connected, as in France, but the state monopoly of instruction prevents the progress of research, for the state is not always able to provide for the increasing needs of research work. The system of grants to the universities, without interference by the state, makes it possible for the American laboratories to take the lead in scientific movements.

Bordeaux Mixture for Wine-Growers' Use

I have previously spoken of the work pursued in France on the use of Bordeaux mixture in the treatment of vineyard diseases.

It had been claimed that the copper had no specific toxic action on the cryptogamic generator of mildew and that the action of pastes was due to their alkalinity.

In the last two years a number of experiments have been made in different parts of France, and the results are concordant. Mere boiling of the lime was in all cases ineffectual. The Academy of Agriculture decided to warn the wine-growers against the use of lime paste, copper paste at present constituting the only efficient treatment.

M. Raphael Bubois thinks, moreover, that the copper is a normal element in the vine. The copper absorbed, whether through the roots or through the leaves, would serve to combat a sort of copper anemia of the plant. The copper would thus confer to the plant an immunity against invasion by the cryptogam. This copper would be in the plant in the form of oxidase or peroxidase as in the hemocyanine of the blood of the snail. This oxidase would insure the defense of the plant against the cryptogamic parasites.

Copper for Conservation of Wood

Along the same line, it is known that for a long time copper has been used in France for the conservation of wood. M. Chavastelon has obtained excellent conservation in using, not only the sulfate, but the bichromate of copper obtained by mixing cold solutions of 6 per cent potassium or sodium bichromate and 6 per cent copper sulfate. Such a solution not only permits the conservation in all the wood, but also makes possible rapid cicatrization of the wounds made in fruit trees, especially wounds of pruning (in apple, walnut, peach, cherry trees, etc.), wounds which, when they are not quickly cicatrized, serve as ports of entry for the animal or vegetable parasites.

Preservation of Foreign Grains and Seeds

It is known that the preservation of grain and seeds of foreign plants is sometimes very difficult. The agricultural stations receive from different parts of the world grains of rare species and these grains very rapidly lose their germinating power; this is particularly striking in the grains containing fatty matter or essential oils. These fatty materials or oils absorb oxygen from the air and it is this oxidation which really takes from the plant its germinating power.

For more than twelve years M. Houdas has been experimenting on the preservation of grains. He has established that the grains of *Jerbera Jamesoni* can be kept in an atmosphere of hydrogen or carbon dioxide, and that under these conditions at the end of twelve years they have not lost their germinating power, this germinating power remaining absolutely constant all the time since the beginning of the experiment (1911). This has also been found true of umbelliferous grains—grains containing an essential oil.

Role of Oxidation in Biological Processes

The part of oxidation in biological phenomena, moreover, has been the object of numerous researches connected with the anti-oxygen notion of MM. Moureau and Dufraisse. In dyestuffs the fixation of oxygen by light has been avoided. It is known that cloth of wool, cotton, or silk is changed more or less rapidly under the action of light, by a change of color. M. Gillet has just shown that phenol in the ortho and para positions has an anti-oxygen action in a dye and prevents its decoloration by light.

Purification of Oils Containing Colloids

In the field of industrial chemistry, I might mention the very interesting work of MM. Marx and Rozies on the purification of oils containing colloidal substances in suspension. This problem was recently studied by the American chemist, Claude Haynes, Jr. MM. Marx and Rozies have solved this problem by combining, in an apparatus called an electro-centrifugal separator, centrifugation and electrolytic precipitation. By passing the colloidal oil solution for five minutes through a current with a strength of 40,000 volts and centrifuging the liquid with a speed of 2700 revolutions per minute for the same length of time, it has been possible, in five minutes, to obtain an optically pure oil.

Substitution of Iron for Lead Water Pipes

The lead mined in France is insufficient to cover its needs. In 1922 we imported over 210 million francs worth of lead. M. Binder suggests that in the future lead be replaced by iron in all water pipe lines. He shows the advantage of this solution of the problem from the point of view of health and economy, since piping costs two and one-half times as much with lead as with iron.

The argument which he gives of the necessity of saving the lead for the manufacture of explosives with a base of nitrate of lead and nitrocellulose, seems to me to have little value.

Chemists Cause Leather Restrictions to Be Removed

Different manifestations of scientific activity are commencing to have their reaction in the decisions taken by the administrations. Thus, the Commission of Leather of the Ministry of Commerce has made France allow the importation of leather and skins coming from the regions where the cattle plague or *aphteuse* fever is raging, with the condition that the leather has been treated with salting or by a chemical preparation.

M. Abt, of Pasteur Institute, has demonstrated that the skins thus treated are no longer dangerous. It is estimated that this measure will reëstablish the market for leather in France.

Report of Carbonization Commission

The Commission of Carbonization of the Ministry of Commerce, inspired by the work of the Congress of Combustible Liquids, has just published its report. The Commission values the reserve of bituminous schists of France at 50,000,000 of tons and the extent of the peat bogs in France at 500,000 hectares. It has established the balance of production of benzene and oil by carbonization as follows:

	Benzene and Light Oils Tons	Heavy Oils Tons
Illuminating gas....	60	135
Cokeries...........	80	130
Gas generators.....	..	15

The cokeries distil 6,500,000 tons of oil and the gas factories 5,000,000 tons. New installations will permit the distillation of 9,500,000 in the cokeries and 6,000,000 in the gas factories. This distillation would give 700,000 tons of resin which we would be able to export.

New Method for Determination of Silica

All chemists know that the gravimetric method of determination of silica in water is very long by reason of the necessity of rendering it insoluble. M. Diener, chief of inspection of water service in the city of Paris, gives a colorimetric method of determination of silica based on the use of molybdate of ammonia in nitric solution. With the aid of this solution he determines colorimetrically the silica, which gives a yellow coloration that can be compared either with solutions titrated with silicate of soda or with picric acid solution standardized with a solution of silica of known titration.

May 30, 1923

Correction—The address of the new offices and laboratories of Skinner, Sherman & Esselen, Inc., of which announcement was made in This Journal, **15** (1923), 540, should be changed to read 276 Stuart St., Boston, Mass.—[Herbert L. Sherman]

Obituary

William Brady

William Brady

William Brady, chief chemist and chemical engineer, Illinois Steel Co., South Works, Chicago, Ill., died Sunday evening, April 22, 1923, at his residence, 7642 Marquette Ave., after a brief illness.

Mr. Brady was born October 28, 1863, at Lafayette, Ind. He was a graduate of Purdue University, class of 1887, and served as assistant instructor of chemistry at that institution from 1887 to 1889. In 1889 he accepted a position as a chemist with the Illinois Steel Company, South Works, and was promoted to assistant chief chemist in 1893. In March, 1893, he left this company to engage in government work at the U. S. Experimental Station at Lafayette, Ind., returning to the Illinois Steel Company in 1894. In 1900 he was appointed chief chemist, and in 1907, chemical engineer.

He had been a member of the American Chemical Society since 1902. He was elected vice chairman of the Chicago Section in 1904, chairman in 1905, councilor in 1909, and a director of the Society in 1913, serving in this capacity until 1916. In 1908 he became a member of the American Society for Testing Materials and the American Electrochemical Society, in 1907, a member of the American Association for the Advancement of Science. He was a member of the Chemists' Clubs of Chicago and New York.

Mr. Brady took an active interest in affairs of the American Chemical Society, giving generously of his time and advice. In 1912, when the Eighth International Congress of Applied Chemistry was held in the United States, Mr. Brady was a member of the executive committee. His untiring energy and service in this work will always be remembered by his associates.

Mr. Brady was an active member of Committee D-5 on Coal and Coke and Committee A-1 on Steel of the American Society for Testing Materials. He also did considerable work for the Bureau of Standards in connection with their standard samples of steel. He was a member of the United States Steel Corporation Chemists' Committee and chairman of several of the subcommittees on standardization of methods of sampling and analysis of iron, steel, and various raw materials and by-products. Mr. Brady was an authority on exploration and valuation work in connection with limestone, fluorspar, and other raw materials used in the manufacture of iron and steel. His fund of knowledge and his executive ability were invaluable. He was active in Y. M. C. A. and welfare work throughout the South Chicago industrial district.

In the passing of "Bill" Brady the American Chemical Society loses a beloved associate, one whose kindliness, interest in his fellow-men, and rugged common sense endeared him to all who came in contact with him.

He is survived by his widow, Mrs. Laura B. Brady, a son, Van W. Brady, and a daughter, Mrs. J. H. Abbott.

L. P. Chase

Personals

Paul M. Giesy has been made director of the Brooklyn Research Laboratories of E. R. Squibb & Sons.

C A. Nash has resigned his position with the Cutler-Hammer Manufacturing Company to accept a position as manager of the Bakelite plant of the Reynolds Spring Co., Jackson, Mich.

L. W. Himmler has resigned his position in the Bureau of Animal Industry to join the research staff of the Cudahy Packing Co., Omaha, Nebr.

Henry Kraemer, of Mount Clemens, Mich., has been elected an honorary member of the Pharmaceutical Society of Great Britain.

Ronier D. Oilar, chemical engineer, has returned from a trip to South America, where he spent more than a year in development and investigational work on vegetable oil, soap, and packing-house industries.

Eric A. Lof, who since 1909 has been employed as an industrial engineer and specialist with the Power and Mining Engineering Department of the General Electric Co., has resigned to accept a position with the American Cyanamid Co., New York, N. Y.

Harold H. Spengler has resigned his position with the Koppers Co., of Pittsburgh, Pa., to accept a position as compounder for part of the mechanical goods of the Goodyear Tire & Rubber Co., Akron, Ohio.

Charles F. Whittemore, of Denver, Colo., sailed on June 6 for Buenos Aires to make installations of apparatus for purifying radium in the Argentine capital. Mr. Whittemore will remain in South America about ten weeks.

F. W. Sullivan, Jr., has resigned from the teaching staff of the Department of Chemistry at the University of Michigan to go into research work with the Standard Oil Company (Indiana), at Caspar, Wyo.

Frank J. Monaghan has been appointed Commissioner of Health for New York City to succeed Royal S. Copeland, who has been elected to the United States Senate. Dr. Monaghan has been sanitary superintendent of New York City for the past five years.

Bradley Stoughton, formerly of Columbia University and later secretary of the American Institute of Mining and Metallurgical Engineers, has been appointed professor of metallurgy at Lehigh University.

John C. Brier has resigned as professor of chemical engineering at the University of Michigan to engage in the development of technical service for the Glidden Company.

Hugh K. Aiken, formerly a member of the Staff of Instruction, Department of Chemistry, Cornell University, has accepted a position with E. I. du Pont de Nemours & Co., Experimental Station, Henry Clay, Del.

H. H. Willard has been appointed full professor of analytical chemistry, University of Michigan, effective in the fall of 1923. Professor Willard has been a member of the staff of the Department of Chemistry for a number of years and has made many valuable contributions in the field of quantitative analysis.

Gerald L. Wendt, now with the Standard Oil Company (Indiana), has been elected an honorary member of the Science Association of the Maharajah's College at Vizianagaram, South India. During the past semester he has been giving a course of lectures on subatomic phenomena at Northwestern University, Evanston, Ill.

R. J. Quinn, formerly of Chicago, has been transferred to the New York office of the Mathieson Alkali Works, Inc., 25 West 43rd St., New York City.

BOOK REVIEWS

The Riddle of the Rhine. By VICTOR LEFEBURE. American Edition. 283 pp. E. P. Dutton & Co., New York. Price, $2.00.

The silence and mystery which have surrounded chemical warfare, the lack of realization of the real forces behind it in Germany, and the failure to grasp the significance of the matter in treaties has led to much misunderstanding and many inaccurate public utterances. This unfortunate state of affairs should be remedied. The English edition of "The Riddle of the Rhine" has already done much to clear the atmosphere, and it is to be expected that this American edition, which is given added authority by a stirring preface by Marshal Foch, will continue the good work. It is a dramatic and at the same time an authentic account of chemical strategy in peace and war, told by one who has had a unique experience of chemical warfare in all its aspects, first with a combatant gas unit on the British front in France, then as Liaison Officer with France and her allies on all chemical warfare matters. Later Major Lefebure assisted Lord Moulton on various questions in connection with the treaty and in surveying the great chemical munition factories of the Rhine. The material which was gathered as a result of these experiences is discussed under the following headings: Explanatory, which gives a general picture of chemical warfare with special reference to the I. G. (Interessen Gemeinschaft). Speaking of this great German chemical monopoly he says: "The existence of this great monopoly raises vital military and economic questions, which are, indeed, the Riddle of the Rhine." Then follow The German Surprise, the story of the first cloud gas attack; The Allied Reaction; Intensive Chemical Warfare; Chemical Warfare Organization; The Struggle for the Initiative; American Developments; Germany's Chemical Policy; Lines of Future Development; Humane or Inhumane; Chemical Warfare and Disarmament; and The Treaty of the Future. The story is well told and the conclusions drawn are in the main sound.

GEO. A. RANKIN

Production and Measurement of High Vacuum. By S. DUSHMAN. 239 pp. 21 × 14 cm. Published by *General Electric Review*, Schenectady, N. Y., 1922. Price, $2.75.

The recent rapid development of such valuable devices as the Coolidge X-ray tube, or the so-called vacuum tube, is a direct outcome of work in the field of very low pressures, and consequently this subject has within a few years become decidedly important, both scientifically and technically. The present volume, which is an expansion and revision of a series of articles published in 1920–21 in the *General Electric Review*, brings together information which heretofore had been scattered, and is provided with many diagrams and tables and with copious references to the original literature. Its scope is indicated by the chapter headings: Kinetic Theory of Gases; High Vacuum Pumps; Manometers for Low Gas Pressures; Sorption of Gases at Low Pressures; Chemical and Electrochemical Clean-Up of Gases at Low Pressures; Theory of Adsorption at Low Pressures. It deals entirely with pressures less than a millimeter of mercury, and particularly with the range from 0.001 millimeter downwards, but is not concerned with the types of vacuum pumps commonly used in engineering practice. This book can be heartily recommended to the increasing number who are interested in high vacuum technic, and should be in every laboratory in which work involving low pressures is being carried on.

JOHN JOHNSTON

Metals and Their Alloys. By CHAS. VICKERS. Large octavo. $6^1/_4 \times 9^1/_4$. xix + 767 pp. 108 illustrations. Henry Carey Baird & Co., Inc., New York, 1923. Price, $7.50 postpaid.

This book started as a revision of "Metallic Alloys," an English book by Brannt which is now out of date, but the alteration has been so great that the result is a work of a different and broader character and properly bears Vickers' name as author rather than as a mere reviser.

The subject matter has three sources—Brannt, current literature, and the experience of Vickers himself. The material from Brannt is of interest more from the historical than the practical viewpoint—e. g., the casting of cannon from gun metal. That from the literature is fairly adequate, although the reviewer believes it would have had a greater value had more references been given. The book makes no pretense of being primarily a scientific treatise, the practical point of view predominates, yet, it will be of even more value to chemists and metallurgists than to foundry foremen, but such technical workers looking for scientific data are hardly given all that they might expect in a work of this nature. However, at less than a cent a page all classes of readers should get their money's worth.

The material that comes from Vickers' own experience is worth more than a cent a page. The discussion of aluminium bronze, manganese bronze, phosphor bronze, red brass, and other casting alloys, not only with regard to the composition of the alloys, their corresponding physical properties, and their uses, but also with regard to melting, deoxidation, casting and gating, and methods of making test bars, covers the field very well indeed.

The discussion of aluminium alloys, wrought brass, and iron and steel is hardly so authoritative or so complete. No chapter on iron and steel could be complete enough to be of much value without taking too much space in a work of this kind. The author has evidently feared to introduce equilibrium diagrams lest he frighten off some of the practical readers for whom he is writing—though one such diagram, Cu-Ni, slipped in. Yet, terms are constantly used which are comprehended with difficulty unless equilibrium relations are understood, and the book loses the systematic presentation that equilibrium diagrams might have given. Still, the author does not hesitate to introduce theory when the theory appeals to him and approvingly mentions Beilby's amorphous cement hypothesis. He quotes an experiment on crushing strength of polished steel balls compared with that of rough-ground or etched balls, to show that the greater strength of the polished balls was due to the layer of amorphous cement formed on the surface in polishing. Most engineers would ascribe the failure of the rough balls to the local concentration of stress on a rough or scratched surface, and the proof is of very doubtful validity.

A good deal of space is used in discussing the history, methods of production, and properties of all the metals in the periodic table, much of which will be used but rarely by the reader. This section contains valuable analyses of metals from different commercial sources and specifications for purity. Besides the subjects already mentioned, and some general chapters, the following are specifically treated: alloys of nickel, tin, lead, mercury, precious metals, magnesium, bearing metals, solders and die castings. A useful chapter on scrap metals is given, as well as one on metal coloring. The A. S. T. M. methods of chemical analysis for Babbitt metals are included.

The book moves along rather jerkily in the second-hand parts, but when it strikes veins of the author's own experience it goes smoothly. It gives a vast amount of information and is quite up to date. No other work covers anywhere near the same ground recent enough to compete with it, and it will be an indispensable reference work for those wishing to know the composition, properties, and uses of nonferrous alloys. It contains a large proportion of the known facts on nonferrous alloys, but the most valuable part of the book is what Vickers gives from his own experience.

The reviewer has noted a few errors of fact, but on the whole, the book seems singularly free from such errors. More facts might be given on many subjects had space permitted. To produce so comprehensive and so correct a book is no small task.

H. W. GILLETT

The Flow of Gases in Furnaces. By W. E. GROUME-GRJIMAILO, translated from the French translation of the original Russian by A. D. WILLIAMS, with extensive appendices by the translator and others. 399 pp. John Wiley & Sons, Inc., New York, 1923. Price, $5.50.

This book is built up about a helpful analogy which regards the flow of hot gases in furnaces as resembling inverted streams of fluid, flowing along the tops of furnaces and flues, over inverted weirs, and exerting quite appreciable pressures as their height increases. The author illustrates many of the points by pictures of kerosene flowing through a furnace model originally filled with water. While the point of view is distinctly stimulating and helpful in many cases, the tendency in the book has been to carry the analogy too far, and overlook the convection and eddy currents which tend to make the hot gas streams mix with the cooler gases, especially at the higher velocities used in boiler settings.

The development of the analogy, the presentation and use of the formulas, for the flow of hot gases over inverted weirs, and the application of these principles to the design of reverberatory furnaces and kilns of various types, are the most valuable portions of the book. Helpful discussion and data on regenerators, hot-blast stoves and open-hearth furnaces are also presented in the book and appendices. On the other hand, the methods given for calculating combustion spaces and resistance through fuel beds are not sound, and the discussion of boiler settings and waste gas boilers is seriously marred by a complete lack of appreciation of the importance of high gas velocities in aiding the transfer of heat. The author and translator appear to consider the ideal boiler setting to consist of a large chamber filled with hot but very slowly moving gas, and they severely criticize the complicated baffle arrangements which have been found desirable in modern water-tube boilers.

The book as a whole gives the impression of a good treatise excessively expanded. There is much unnecessary repetition between the 18 pages of preface, etc., the 150 pages in the main portion, and the 250 pages of appendices. Many of the tables and data in the appendix are readily available elsewhere, and have a degree of detail and number of decimal points quite unwarranted by the kind of calculations involved. Some of the sections in the appendix appear to go into unnecessary detail, especially in view of their almost total neglect of important items such as heat transfer.

As indicated above, however, the fundamental hydraulic concept and its clear exposition by the author are distinctly helpful in many connections, and should be read by anyone concerned in the design of metallurgical furnaces and similar problems. Its value in designing boiler and still settings is much less apparent.

The double translation does not appear to have interfered with the smoothness and clarity of the discussion, though the continual use of "calorific intensity" in place of "temperature" should be criticized.

ROBERT E. WILSON

Patents—Law and Practice. 2nd edition, 1922. 56 pp. **Trade-Marks—Trade Names, Unfair Competition.** 3rd edition, 1922. 46 pp. Published by Richards & Geier, Patent Attorneys, New York. (Gratis.)

The average American chemist knows but little patent law. It is natural that few chemists should be enough interested in man-made laws to wander through elaborate treatises on the subject. Every inventor has, however, a mild curiosity to find out the rudiments of this necessary evil, the same sort of curiosity as he shows towards the income tax laws.

Richards & Geier, patent attorneys, should not only be complimented but thanked for their recent booklets on patents and trade-marks.

The booklet on patents gives a clear and concise description of the process of patenting in this country and some of the outstanding features of the process in foreign countries. They have been "indiscreet" and tabulated the various charges—working, taxes, assignments, translations, etc. They have not been indiscreet enough; the reviewer would have them give a table of "total costs" for a patent in the various countries. Our own patent office would gain by this exposition.

There is a deep mystery surrounding trade-marks, which laymen rarely realize. If Richards & Geier's little book on this subject can explain to the reader's satisfaction just what is a trade-mark and what is not, it will have served a worthwhile purpose.

D. B. KEYES

Chemical Technology and Analysis of Oils, Fats, and Waxes. By J. LEWKOWITSCH. 6th edition, revised by GEORGE H. WARBURTON. Volume III. Macmillan & Co., Ltd., St. Martins St., London, 1923.

This edition of Volume III follows the well-known fifth edition so closely that it is unnecessary to give a detailed description of its contents. The present volume contains 25 pages more than that of the previous edition. Some of the additional pages were required to bring the tabulations of statistical data of the former edition to 1920 or 1921. A number of other tables as well as some descriptive matter have been added in order to bring certain subjects to date. Also new references both to the chemical and to the patent literature will be found in addition to those previously given. The appendix contains valuable information and references to investigations which were published after Volumes I and II had gone to press. It should be observed that the index given in this volume lists, under the appropriate headings, the contents of the appendix.

Considerable space in a number of the sections is still utilized, as in the former edition, by descriptions of various obsolete or impractical methods of manufacture which could have been replaced to advantage by a description of some of the newer processes and equipment employed in connection with the solvent extraction, the refining, and the deodorization of vegetable oils for edible purposes. Furthermore, there are quite a number of statements taken from previous editions which do not apply to the present commercial practice, such as, for example, the separation and removal of water (condensed steam) after the deodorization of an oil. Another statement is that corn (maize) oil is only used in the margarines of lower quality on account of its grainy flavor, which is difficult to remove. The modern deodorizer gives corn oil entirely free from grainy taste. In connection with the discussion of vegetable margarines, it was observed that no reference was made to the use of peanut oil along with coconut or palm kernel oils in the manufacture of the so-called nut margarines, which is rapidly assuming large proportions.

In view of the great amount of information contained in the three volumes of this comprehensive work, it well deserves a place both in the technical reference library and in the working library.

GEORGE JAMIESON

Synthetic Resins and Their Plastics. By Carleton Ellis. 514 pp. The Chemical Catalog Co., Inc., New York, 1923. Price, $6.00.

Any one interested in the manufacture or application of synthetic resins should find this volume of very great value. The book is a comprehensive presentation of the subject, well written and well illustrated. Many of the chapters have been reviewed and revised by well-known authorities, and in general the subject has been brought up to date.

Molding resins of the Bakelite type have received the most attention, although coumarone, ketone, furfural, sulfur, nitro-resins, and other types, as well as chlorinated rubber, are considered. Three chapters are devoted to rosin esters and modified natural resins and their application in the varnish industry.

The last third of the book deals with the technic of plastic molding. Various types of molds, presses, and other apparatus, together with descriptions of their operation, are given in detail, with many illustrations and diagrams. A detailed description of the hot and cold processes is given and the advantages and disadvantages of each are discussed.

The last chapter deals with the tests which are applied to molded products.

A complete author's and subject index is included, and copious references to the literature are given throughout the book.

F. B. LaForge

The Destructive Distillation of Wood. By H. M. Bunbury. 320 pp. 107 illustrations. 115 tables. Benn Brothers, Ltd., London, 1923. Price, 35s. net. D. Van Nostrand Co., New York. Price, $8.50.

It is rather surprising that, in view of the importance of the industry of destructive distillation of woods, no comprehensive treatment on the subject has previously been compiled. While the field of coal distillation has been thoroughly covered by several treatises, Bunbury's work is the first of its kind for wood.

The book opens with a brief discussion of the physical and chemical properties of wood, and while the majority of the readers of the work may not be interested in a constitution for either cellulose or lignin, it seems to the reviewer that such discussion is highly desirable in a work of this kind. Then follow chapters on the thermal decomposition reactions and the factors which influence these reactions. The remainder of the work is devoted to the discussion of the commercial processes, apparatus, and operations. The production of charcoal, calcium acetate, wood alcohol, wood turpentine, pine oils, wood tar, wood pitch, etc., is discussed in detail. Numerous illustrations of the apparatus used in these processes are given, and the yields and properties (such as solubility, etc.) of the distillation products are given in tabular form. In view of the present interest in waste utilization, the chapter on the destructive distillation of small wood and wood waste is especially timely. This chapter is also indicative of the "up-to-dateness" of the work, including as it does a discussion of Stafford's recently patented process, which utilizes the heat liberated by the exothermic reactions involved in the thermal decomposition of wood to initiate the decomposition of a fresh charge, and that of the production of gas (illuminating and power), which assumed special importance during the European war.

This work is a very important contribution to the subject of destructive distillation in general and to that of wood distillation in particular. It should prove of great interest to all those engaged in the industry, and to chemists and technologists other than those engaged directly in the industry. The book is well printed and contains a minimum of typographical errors.

Clarence J. West

Blanchiment, Teinture, Impression, Apprets. By P. Lederlin. 539 pp. Bailliere et Fils, Paris, 1923. Price, paper 45 fr.; bound 55 fr.

This well-printed volume is devoted to the bleaching, dyeing, printing, and finishing of cotton, other fibers being mentioned under printing only. The first 89 pages are devoted to the chemical and physical properties of cotton and to bleaching, 279 pages are allotted to dyeing, printing is described in the next 146 pages, while in 25 pages the author covers the entire subject of finishing. A goodly number of excellent illustrations round out the text.

Apparently little use is made in France of the vat dyes, either in dyeing or printing, if one is to judge from the space devoted to them. While some attention is given to skein dyeing, the author rightly states that the work of dyeing tends to be accomplished more and more by machines and less by manual labor. Yet when we read that certain mechanical driers are interesting because they permit of drying 100 to 200 kgs. per hr. at 60 to 70° C., and compare this with a production of 1000 lbs. or more per hour from American driers, we must conclude that the author has something to realize as to production.

Under recovery of sodium hydroxide from waste, dilute mercerizing liquors, no mention is made of using them in conjunction with liquid chlorine to make sodium hypochlorite, a process which does away with any need of evaporation.

Nearly three pages which are devoted to a table showing the commercial names for dyes adopted by various dye makers might have been more usefully employed, for example, in giving more about finishing.

The chapter on the practical processes of dyeing is subdivided according to shades rather than according to dye classes.

The chapter on the theory of dyeing and on sampling shades is well worth reading. Many formulas for printing pastes are given.

The book as a whole is interesting as giving light on present-day practice in France rather than as offering help and inspiration to the American dyer.

Miles R. Moffatt

A Textbook of Filtration. By C. L. Bryden and G. D. Dickey. 376 pp. Chemical Publishing Co., Easton, Pa. Price, $5.50.

The first chapter deals with the principles of filtration. The compilation is rather confusing and perhaps should have been reviewed prior to publication by some one competent to pass upon this difficult subject. A few errors and contradictions occur. A number of photomicrographs of precipitates are shown which are quite interesting. No mention is made of adsorption, undoubtedly an important factor in filtration.

Chapter 2, History of Filtration, is really a history of filters and is quite good. The authors include some apparatus which are not filters.

Chapters 3 to 13, according to the introduction, deal with various types of filters. As a matter of fact, 30 to 40 per cent of the apparatus described are not filters at all. For example, hydraulic presses, oil extractors, expellers, and oil separators are considered. Curiously, even light, color, and radio "filters" are included. The descriptions are perhaps a little better than can be found in trade catalogs. The leaf and rotary filters are handled best, although the reader is apt to form an exaggerated idea of their real importance in the industrial field. Plate and frame filters are poorly handled, which is unfortunate in view of the dominating position which this class of filter holds in the world to-day. The statement that it is difficult to wash efficiently in filter presses is not correct. No mention is made of the Plauson or of the Haubold filters.

Chapter 13 deals with coagulants and filter aids, and is well handled, although certain debatable statements are made.

Chapter 14, Filter Media, meaning filter bases, is treated very well with the exception of the matter dealing with the effect of filter supports. The conclusion that the permeability of cloths is greatly influenced by the character of ordinary supporting surfaces is evidently erroneous, as can be demonstrated by simple tests. The effect of adsorption is not considered. No mention is made of filter paper.

Chapter 15 deals with operating data. Very little information not generally known is given, while specific data refer to tests on a few substances not of general interest. A curve in Fig. 231 compares washing in theory, in open-tank filter, and in plate and frame filter, but neglects to state whether simple or thorough washing was used in the latter; hence, the comparison is meaningless.

Chapter 16, Auxiliary Equipment, covers most filter equipment under the head but omits the pressure diaphram pump and the montejus.

An appendix which follows contains information which can be found elsewhere.

In general, while this book is undoubtedly the best work on the subject to-day, it is lacking in specific information. Cost data and rates of flow for various well-known substances are absent. It is doubtful if a person with a filtration problem to solve would get much satisfaction from this book alone. Should you wish, for example, to find a suitable filter for linseed oil, you would look in vain in this book for the proper type, the area required, the filter base to use, the cost, kind of pump, pressure, etc.

The text refers in a number of places to letters which do not exist on cuts, as on page 208.

D. R. Sperry

Wave Length Tables for Spectrum Analysis. By F. Twyman, 116 pp. Demy 800. Adam Hilger, London, England. 1923. Price, 7s. 6d.

This work is from a series of seven publications of the Hilger Company, one of these being the excellent booklet by Silberstein on the "Quantum Theory." In the preface the author states:

> For the purposes of spectrum analysis two kinds of tables are required. The one should give, with an accuracy beyond question, the wave lengths of radiations easily reproducible in the laboratory; the other should give the wave lengths of distinctive lines of the elements, for the purpose of identification.

The chief wave lengths from 2375 to 8495A are tabulated for more than forty elements, usually to the nearest 0.1 Ångstrom, this being the precision which the author considers satisfactory. Dr. Meggers, however, has found that even for satisfactory identification purposes, the wave lengths should be known to 0.1A. Many of the tables are collected from the pioneer works of early investigators before the precision methods of modern spectroscopy were known—for example, from the work of Hartley dating from 1884. Thus, while the wave lengths of the first pair of the principal series of copper are known to be 3247.550 and 3373.967, they are here listed as 3246.9 and 3273.2, respectively. In fact, it is doubtful if in many of the tables the lines tabulated may be relied upon to better than several tenth Ångstroms, surely a severe criticism of the work in view of the vast quantity of precision data now readily accessible. In spite of these inaccuracies the book possesses much of merit. The tables give the prominent wave lengths for various degrees of concentration of the element down to the point where only the *raies ultimes*, or persistent lines, appear. The persistent lines of Pollok and Leonard are arranged in order of wave length paralleled by the elements they characterize. A complete list of *raies ultimes*, as found by de Gramont, are compiled in two ways, according to the element, and according to wave length. Six pages are transcribed from a paper by Plaskett on wave lengths for use in determinations of stellar radial velocities. These are given to 0.001 Å., as are also the secondary and tertiary standards adopted and recommended for adoption by the International Solar Union. The latter include eight pages of tables for iron, neon, and helium. Data are given for the reduction of the Rowland to the international scale and for the correction from air at 15° C., 760 mm., to vacuum. A good bibliography is appended to the book and the references to the (older) literature are quite extensive. Practically the entire work consists of clippings or quotations, all original comments being in italics. These are arranged in a logical order and form interesting reading matter. The book will be especially useful in the collegiate undergraduate laboratory, and for analytical work as a treatise supplementary to the more precise, but less convenient, existing tables.

Paul D. Foote

A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. III—Copper, Silver, Gold, Strontium, Barium. By J. W. Mellor, D.Sc. 927 pp. Longmans, Green & Co., London, 1923. Price, $20.00 per volume.

Before reviewing in any detail the third volume of this important work, it may be well to comment briefly on the reception which has been accorded the first two volumes, as they have been widely reviewed, not only in the scientific and technical journals, but also to some extent in the popular press.

The first impression, which appears to be almost universal, is one of amazement and admiration that any one individual should undertake and be able to carry on such a tremendous task as the compilation of this treatise (it is to occupy six or seven volumes). The reviewer is glad to add his tribute to the courage, industry, and wide knowledge which the author has displayed.

Concerning the content of the work, opinions have differed somewhat according to the viewpoint which has been taken.

The work follows very closely the arrangement of the earlier textbook, "An Introduction to Modern Inorganic and Theoretical Chemistry." This involves the frequent insertion of very general theory into chapters dealing with specific substances, which in the opinion of the reviewer constitutes a handicap to the use of the book for pure reference purposes; on the other hand, it makes the volumes more readable and interesting to the student who may turn to them for general reading. It seems hardly necessary to comment further on Volumes I and II, as reviews of these are readily available.[1]

Volume III contains a much smaller proportion of theoretical discussion than Volume I, and somewhat less than Volume II, although in the chapter on gold, colloids are discussed. The chemistry and properties of copper, silver, and gold are treated separately and in characteristic detail; the alkaline earths are treated simultaneously with comparison and contrast.

As in the former volumes, the historical method of treatment is followed and an enormous number of facts are presented. The inclusion of a large number of the qualitative or semiqualitative statements of the older writers adds to the completeness of the references, but results frequently in contradictory statements which may lead to some confusion when the book is used for reference. The reviewer is doubtful of the value of such typical statements as (p. 875): "J. A. Volcker found that a liter of cold water dissolves 31 mgrm. of calcined, and 79 mgrm. of precipitated calcium phosphate in seven days;" when followed by a detailed statement of the exact work of Cameron and others on this somewhat complicated question.

Errors and misprints seem to be rare; references to the literature are extremely full, though their location at the end of each section makes them not altogether easy to use. Perhaps a complete author index is to appear in a later volume.

The work is unquestionably the most complete source of information existing in English, and the remaining volumes will be awaited with great interest.

Graham Edgar

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[1] *J. Am. Chem. Soc.*, **44** (1922), 1836, 2661. *J. Phys. Chem.*, **26**, (1922), 591.

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

May

Peanut oil from France has practically displaced **cottonseed oil** and **corn oil** from the United States in the Guadeloupe market. American oils are considered superior to the French oil in body and flavor, but this superiority is not regarded as sufficient to overcome the handicap of higher price. (P. 351)

Experiments conducted in the Philippines have shown that **alcohol** as **fuel** for trucks is successful, but such is not the case with passenger cars. Besides the offensive odor, the carburetors do not supply enough air, and the economy is not sufficient to warrant passenger-car users in changing their carburetors. (P. 356)

Germany, in 1922, produced 6,000,000 kilos of **artificial silk.** The average monthly production at the beginning of the year was 350,000 kilos, but by the end of the year it had reached 600,000 kilos. (P. 365)

The Chilean **sulfur industry** is reviewed, including a description of the principal mines, the growth of production, and a prediction as to the future of the industry. (Pp. 370–1)

The output of Italy's **superphosphate** plants for 1922 is estimated at 900,000 tons, against 678,000 tons in 1921, and 665,000 tons in 1920. Her present potential capacity, however, is estimated at from 1,300,000 to 1,400,000 tons a year. The manufacture of **sulfate of ammonia** from synthetic ammonia by the methods of the Italian chemists Casale and Fauser is now being undertaken. (P. 371)

Japan has restricted the output of **artificial fertilizers** for the remainder of 1923 by 35 per cent of capacity production. (P. 372)

Since December, 1922, great activity has been reported in the Aden **gum** market, particularly gum frankincense. (P. 372)

Apricot gum can be used as a substitute for gum arabic in all the cruder processes in which the latter substance is employed. (P. 372)

The export duty on crude **mineral oil** has been increased from 50 to 150 Polish marks per net kilo, by a joint order of the Polish Ministers of Finance. (P. 396)

The outstanding facts brought out in the review of the world trade in the **essential oils of citrus fruits** are that Italy takes first place in world production; essential oil production is an important industry of Mediterranean countries and British West Indies; and the United States imports of citrus oils show an increase since the war. (Pp. 417–9)

A maximum of 36,020 long tons of Ceylon-produced **rubber** may be exported from the island during the year ending October 31, 1923. The amount is well below shipments for the past four calendar years. (P. 428)

The standard production of **rubber** in the Federated Malay States has been assessed at approximately 150,000 tons. For the whole of British Malaya statistics show a standard production of 267,000 tons, of which 160,200 may be exported. (Pp. 428–9)

The total production of **iron ore** in France in 1922 was 20,831,993 metric tons, which is a considerable increase over production for 1921. (P. 442)

A large deposit of **kaolin,** said to contain at least 200,000 tons and extending deep into the earth, is said to have been discovered in eastern Finland. (Pp. 442–3)

A recent Argentine **petroleum** decree provides for more stringent regulation of the operation of petroleum concessions in that Province. (P. 444)

The government of Madras has appointed a committee of ten men, composed of government officials and civilian experts, to examine the steps which are desirable to further the development of the **leather industry** in the Presidency of Madras, with special reference to the present constitution and aims of the Leather Trades Institute. (P. 447)

The exportation from France of **sulfate of ammonia** is again under restriction. (P. 453)

The **quicksilver industry** of Japan is reviewed. (P. 489)

The **chemical industry** is generally rated as occupying third place among German industries in total exports in gold values, it being only exceeded by the heavy metals industry and the textile industry. (Pp. 499–500)

The **chemical trade** of the Netherlands in 1922 is reviewed. (Pp. 500–1)

Under the **restrictive rubber scheme** now effective in the Federated Malay States, the standard production of estates of 25 acres or less amounts to 28 per cent of the total standard production of all estates. (P. 505)

There is considerable optimism in Bolivia over the possible revival in the **rubber industry.** (P. 505)

The prosperity which struck the British **paper industry** during the latter part of 1922 has continued through the first three months of 1923. (P. 509)

Top prices appear to have been reached for German **pulp wood** from coniferous timber. (P. 510)

It is reported that a discovery in the manufacture of high-grade **paper** now makes it possible to eliminate the brown stain, which hitherto has confined the use of New Zealand flax to the making of wrapping paper and millboard. (P. 510)

Mangrove sources, development, and trade are described. Although not an exploiter of this product, the United States consumes important quantities of the bark and extract, obtaining its supplies chiefly from the African and Asiatic markets. The **tannin content** of the bark ranges from 5 to 48 per cent, and of the extract from 48 to 72 per cent, depending on the country of origin. (Pp. 552–4)

The value of **chemicals** and **allied products** exported from the United States during the first quarter of 1923, according to preliminary figures, increased 17 per cent over the corresponding period of 1922. These increases in value ranged from 19 per cent in the case of medicinal and pharmaceutical products to 130 per cent in the case of wood and denatured products, and also included coal-tar products; naval stores; paints, pigments, and varnishes; and perfumery, cosmetics, and other toilet preparations. (Pp. 554–6)

The Australian **gypsum industry** is reviewed. (P. 563)

The first shipments of **antimony ore** for several years from San Luis, Mexico, were made to the United States during April. (P. 563)

Czechoslovakia has announced that in the future the sales price of **tin** manufactured in the State ovens will be equivalent to the price in the London market, plus the Czechoslovak import taxes. The price of **antimony** will be similarly fixed. (P. 563)

Chilean markets for **petroleum products** are described. Strange to say, there is no domestic production of crude petroleum, and all petroleum products consumed must be imported. (Pp. 571–2)

Certain specified Portuguese lands have been declared free for registering for **petroleum research** and explorations. (P. 572)

The Petroleum Division of the Bureau of Foreign and Domestic Commerce has available for consultation copies of the translation of the law relating to the exploitation of **petroleum deposits** in the republic of Panama, which was approved on April 6, 1923. (P. 572)

The consumption of **petroleum products** in Poland during 1922 amounted to 245,140 metric tons, an increase of 27,040 tons over 1921. (P. 572)

There is a demand for **paraffin** in the Vera Cruz district to be used in the manufacture of candles. (P. 572)

STATISTICS OF EXPORTS TO THE UNITED STATES

- Athens—(P. 399)
  - Chrome ore
  - Magnesite ore
  - Magnesite ore (calcined)
  - Olive oil
- Saloniki—(P. 399)
  - Opium
- Palestine—(P. 400)
  - Olive oil
- Cyprus—(P. 527)
  - Umber, calcined
  - Umber, raw
- Netherlands—(Pp. 500–1)
  - Magnesia
  - Glue
  - Gelatin
  - Quinine
  - White zinc
  - Lithopone
- Sumatra—(P. 505)
  - Crude rubber
- Great Britain—(P. 509)
  - Printing paper
- Teheran, Persia—(P. 527)
  - Gum tragacanth

CURRENT PUBLICATIONS

NEW BOOKS

Activated Sludge Studies, 1920 1922. Bulletin No. 18. 150 pp. Division of the State Water Survey, Urbana, Ill.

Agricultural Bacteriology: Textbook of Agricultural Bacteriology. F. Lohnis and E. B. Fred. 283 pp Illustrated. Price, $3.00 net. McGraw Hill Book Co., Inc., New York.

By-product Coking. G. Stanley Cooper. 192 pp. Price, 12s. 6d. Benn Bros., Ltd., London.

Chemical Industry: Annual Report of the Society of Chemical Industry on the Progress of Applied Chemistry. Vol. VII. 586 pp. Society of Chemical Industry, London.

Coal and Allied Subjects, Being Bulletins 1 to 10 of the Lancashire and Chesire Coal Research Association. F. Sinnatt. 205 pp. Price, 15s. net. H. F. & G. Witherby. London.

Electrochemistry Related to Engineering. W. R. Cooper. *Edited* by Bertram Blount and W. H. Woodcock 176 pp. Illustrated. Price, 10s net. Constable & Co., Ltd., London.

Handbook of Testing. Vol. II. The Theory of Prime Movers. C. A. Middleton Smith. 299 pp. Illustrated. Price, 22s. 6d. net. Constable & Co., Ltd., London.

Handbook: Kent's Mechanical Engineers' Handbook. Robert T. Kent, Editor-in-Chief. 10th edition, rewritten. 1900 pp. Price, $6.00. John Wiley & Sons, Inc., New York.

Hydrochloric Acid: The Manufacture of Hydrochloric Acid and Saltcake. Alexander Charles Cumming. 423 pp. Price, 31s. 6d. Gurney & Jackson, London.

Industrial Fatigue: Third Annual Report of the Industrial Fatigue Research Board, to December 31, Including Personal Contributions from Investigators. Medical Research Council. 83 pp. Price, 2s. H. M. Stationery Office, London.

Industrial Furnaces. Vol. I. W. Trinks. 319 pp. Illustrated. Price, $4.50 net. John Wiley & Sons, Inc., New York.

Phase Rule. A. C. D. Rivett. 204 pp. Price, 10s. 6d. The Clarendon Press, Oxford, England.

Physics in Industry. Archibald Barr Sir James Alfred Ewing, and Clifford C. Paterson. 59 pp. Price, 2s. 6d. Henry Frowde & Hodder & Stoughton, London.

Relativity: Four Lectures on Relativity and Space. Charles P. Steinmetz. 130 pp. Illustrated. Price, $2.00. McGraw-Hill Book Co., Inc., New York.

Soap: La Fabrication des Savons Industriels, Émulsions pour l'Ensimage, et Huiles Solubles. R. Ehrsam. 2nd edition, revised and enlarged. 305 pp. Illustrated. Price 30 fr. 50. Dunod, Paris.

Sulfuric Acid: Raw Materials for the Manufacture of Sulfuric Acid and the Manufacture of Sulfur Dioxide. Wilfrid Wyld. 558 pp. Price, 36s. Gurney & Jackson, London.

Systematic Organic Chemistry. W. M. Cumming, I. Vance Hopper, and T. Sherlock Wheeler. 656 pp. Price, 27s. 6d. Constable & Co., Ltd., London.

Technical Mathematics. Harry M. Keal, Nancy S Phelps, and Clarence J. Leonard. Vol. I. 231 pp. 145 figures. Price, $1.50. Vol. II. 271 pp. 306 figures. Price, $1.75. Vol. II 138 pp. 136 figures. Price, $1.25. John Wiley & Sons, Inc., New York.

Tested Methods of Nonferrous Metallurgical Analysis. Seymour Pile and Reginald Johnson. 128 pp. Price, 7s. 6d. net. H. F. & G. Witherby, London.

Underwriters' Laboratories: A Symbol of Safety—An Interpretative Study of a Notable Institution Organized for Service, not Profit. Harry Chase Brearley. Price, $2.50. 290 pp. Doubleday Page & Co., New York.

Wood: L'Usinage du Bois, Puissance Requise par les Machines a Bois, Dynamique Machines à Grande Vitesse. J. Petitpas. 236 pp. Price, 21 fr 50. Dunod, Paris.

Wood Distillation. L. F Hawley. American Chemical Society Monograph Series. Price, $3.00. Chemical Catalog Co., Inc., New York.

RECENT JOURNAL ARTICLES

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High Frequency Induction Furnace. An 11-page leaflet published by the Ajax Electrothermic Corp., Trenton, N. J.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

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Additions, Removals, and Changes in Permissible List of Explosives from December 31, 1922, to March 15, 1923. S. P. Howell. *Reports of Investigations* **2467.** 4 pp. Issued April, 1923.

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MARKET REPORT—JUNE, 1923

[Supplied by Drug & Chemical Markets]

Heavy chemicals, intermediates, medicinal chemicals, and fatty oils have all shown a continued downward tendency during June. The average movement of prices toward lower levels approximated 2 per cent for the month. Buying has been limited to small lots for immediate use, consumers showing increased caution in the face of the prices under competitive pressure. There is practically no buying ahead, deliveries on contracts at the present time being made on agreements signed during the first three months of the year or last December. A goodly portion of the American manufacturers keep plants running full time on old contracts. Those hardest hit by the slow business are the importers with accumulated spot stocks on their hands which they are now unable to move.

Many consumers are still operating on stocks purchased earlier in the year, coming into the market only when absolutely necessary and confining business to small quantities. Orders are usually accompanied by immediate delivery instructions. With the exception of a very few items, supplies of chemicals are plentiful. Imported materials, especially, are abundant, and many holders have been forced to sacrifice their profits, and in some instances take losses, in order to sell their goods. Prices of nearly all imported chemicals have become easy. Copper sulfate is very weak due to large importations and practically no market for the material. Domestic manufacturers have covered the agricultural districts quite thoroughly, and importers have been forced to sell as low as $4^1/_2$ cents per lb. while domestic material has been selling at $5^3/_4$ cents per lb.

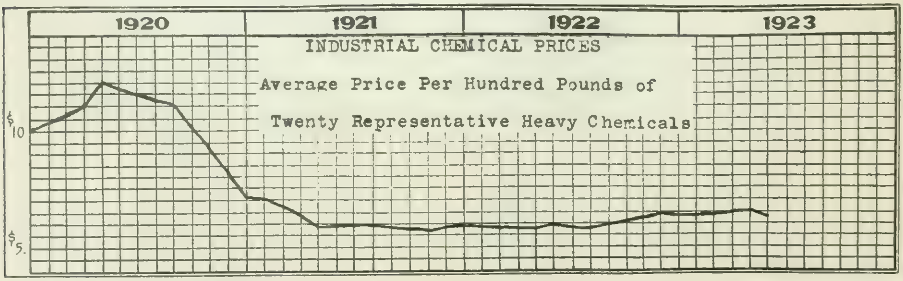
Caustic potash is another item on the list for which there has been a slow demand. A large shipment recently arrived which was sold well under the spot market price. This weakened the market and caused a drop from $8^1/_4$ to $7^1/_2$ cents per lb. Domestic caustic potash has been moving well since its manufacture was begun a few months ago, with prices fully a cent a pound higher than imported potash. Yellow prussiate of soda has been falling steadily and manufacturers have reduced their prices in order to compete with the importers for the little business available. Potassium permanganate suddenly dropped 5 or 6 cents a lb. during June after enjoying a steady advance from 16 up to 25 cents a lb. Potassium carbonate is also lower.

While there has been a slowing up in activity with manufacturers, there has been enough business passing, also with the regular contract deliveries, to keep the plants operating at nearly capacity. Heavy acids have been moving steadily into all consuming channels. Sulfuric acid and oleum have been in limited supply. Oxalic acid is higher and firm. Bleaching powder demand has fallen off as mills entering the summer months do not carry as large stocks. Prices are lower in some directions. Arsenic is passing through its quiet season, little trading being done, and prices are easy. Some material has been arriving from abroad at regular intervals, but supplies are not large. The calcium arsenate situation has been very perplexing. The late and cold spring in the South retarded the planting and growth of the cotton plants three to four weeks. Dealers, both in the South and in New York, have been holding stocks of arsenate waiting for the appearance of the boll weevil in the cotton fields and the consequent demand for insecticides. In the local market many holders have been offering at low prices in order to move stock on which payments have become due. The weevil is reported to have appeared in the cotton fields and demand is expected to begin soon. Sodium and potassium bichromates are in good demand and prices firm. Glauber's salt is higher. Methyl acetone has been advanced. Tin crystals are lower for June.

Crude coal-tar products have been gradually becoming more plentiful with prices lower in most items. Benzene and toluene are quoted lower. Demand for naphthalene has fallen off and prices are easier. Phenol prices are holding firm at 50 to 52 cents per lb. The manufacture of synthetic phenol has been begun by an American manufacturer who is producing 5000 lbs. per day. This is the first American production in five years. Xylene is in slightly better supply. Intermediates have been quiet since the demand for dyestuffs has fallen off.

Weakness in animal and vegetable oils continued throughout the month with declines in nearly all items. Menhaden fishing operations have begun and prices are held at high levels owing to the small catches caused by labor shortage. Turpentine continued its decline of the previous month but recovered slightly towards the close. Rosin prices are also lower.

Quicksilver was quoted higher at mines during June at £10 19s. 6d, while spot London metal held at £10 5s. per flask. Demand at the moment is limited to small buying. The trade looks for firmer prices since the mines are closed down and the stocks are said to be none too heavy to take care of demands for the next few months.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

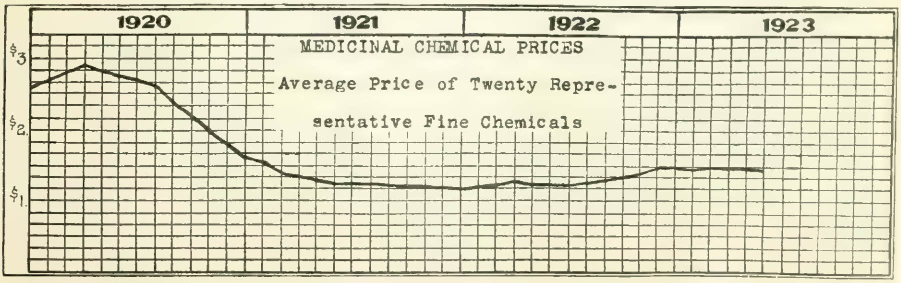
INORGANIC CHEMICALS

	June 1	June 15	Jan. 1923
Acid, Boric, cryst. bbls.......lb.	.11	.11	.11½
Hydrochloric,comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb	.65	.65	.65
Nitric, 42°, cbys. c/1 wks.lb.	.05¾	.05¾	.06
Phosphoric, 50% tech....lb.	.08	.08	.08
Sulfuric, C. P...........lb.	.09	.09	.07
66° tks. wks.......ton	15.00	15.00	15.00
Oleum, 20%.......ton	19.00	19.00	18.00
Alum, Ammonia. lump.......lb.	.03½	.03½	.03½
Potash, lump...........lb.	*.03¼	*.03¼	*.03½
Chrome............lb.	.05½	.05½	.05½
Soda, ground...........lb.	.04	.04	.04
Aluminum Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd..lb.	.09	.09	.09½
Chloride, white gran.....lb.	.07½	.07½	.07½
Ammonia, anhydrous........lb.	.30	.30	.30
Ammonia Water, drums, 26°.lb.	.07½	.07½	.07½
Arsenic, white..............lb.	.14½	.14	.15½
Barium Choride............ton	*85.00	*85.00	*92.50
Nitrate................lb.	*.08	*.08	*.07½
Barytes, white.............ton	33.50	33.50	33.50
Bleaching Powd., 35%, works .... 100 lbs.	2.00	2.00	2.15
Borax, cryst., bbls..........lb.	.05½	.05¼	.05½
Bromine, pure, wks..........lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b. N. Y..................ton	24.56	24.50	24.50
Chlorine, liquid.............lb.	.05¼	.05¼	.05¼
Copper Sulfate......... 100 lbs.	5.75	5.65	6.25
Iodine, resublimed..........lb.	4.55	4.55	4.50
Lead Acetate, white crystals..lb.	.14	.14	.13
Nitrate................lb.	.22	.22	.22
Red.............. 100 lbs.	11.40	11.40	10.60
White (Carb.)..........lb.	.09¾	.09¾	.08½
Lime, live and hydrated, bbl..lb.	.01½	.01½	.01½
Oyster shell............lb.	.03	.03	.03
Lime Acetate.......... 100 lbs.	4.00	4.00	3.50
Magnesium Carbonate, tech..lb.	.08	.08	.08
Magnesite, calcined.........ton	55.00	55.00	55.00
Phosphorus, yellow..........lb.	*.35	*.35	*.28
Red....................lb.			*.30
Plaster of Paris, tech ....bbl.	3.30	3.30	3.30
Potassium Bichromate.......lb.	.11½	.11½	.10
Bromide, imported......lb.	.16	*.16	.14½
Carbonate, calc.,80–85%.lb.	*.06½	*.07	*.05½
Chlorate, cryst..........lb.	*.07½	*.07½	*.05½
Hydroxide, 88–92%.....lb.	*.07¾	*.07¾	*.08
Iodide, bulk, U. S. P.....lb.	3.75	3.75	3.60
Nitrate................lb.	.06½	.06½	.06½
Permanganate, U. S. P...lb.	*.19	*.19	*.16
Prussiate, red...........lb.	*.72	*.72	*.90
Yellow.............lb.	*.36	*.36	*.38
Salt Cake, bulk............ton	26.00	26.00	28.00
Silver Nitrate...............oz.	.44	.44½	.44
Soda Ash, 58%, bags....100 lbs.	*2.00	*2.00	*2.00
Caustic, 76%, N. Y. 100 lbs.	3.70	3.70	3.50
Sodium Acetate.............lb.	.05½	.05½	.07¼
Bicarbonate....... 100 lbs.	2.25	2.25	2.00
Bichromate.............lb.	.08½	.08½	.07¾
Bisulfite, powd..........lb.	.04	.04	.04
Chlorate...............lb.	.06½	.06½	.06½
Cyanide, 96–98%.......lb.	.23	.23	.23
Fluoride, tech...........lb.	.09½	.09½	.09½
Hyposulfite, bbls... 100 lbs.	2.90	2.90	3.60
Nitrate, 95%...... 100 lbs.	2.50	2.50	2.57½
Nitrite.................lb.	.08	.08	.08½
Prussiate, yellow........lb.	.16	.16	.18½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40° ....100 lbs.	.80	.80	.80
Sulfide, 60%, fused......lb.	.05	.05	.05
Strontium Nitrate...........lb.	*.12½	*.12½	*.08¾
Sulfur, flowers.........100 lbs.	3.00	3.00	3.00
Crude, mines......long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n....lb.	.12½	.12½	.10¼
Oxide..................lb.	.50	.50	.43
Zinc Chloride, U. S. P........lb.	.25	.25	.20
Oxide, bbls.............lb.	.07½	.07½	.07½

* Resale or Imported (not an American maker's price).

ORGANIC CHEMICALS

	June 1	June 15	Jan. 1923
Acetanilide, U. S. P., bbls....lb.	.35	.32	.35
Acid, Acetic, 28 p. c.... 100 lbs.	3.17½	3.38	3.17½
Glacial ....100 lbs.	12.50	12.75	12.05
Benzoic, U. S. P.........lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drums.............lb.	.55	.55	.32
50- to 110-lb. tins...lb.	.57	.57	.34
Citric, crystals, kegs.....lb.	*.52	*.52	*.48½
Oxalic, cryst., bbls., wks.lb.	.13¼	.13½	.13½
Pyrogallic, resublimed...lb.	1.55	1.55	1.55
Salicylic, U. S. P.........lb.	.40	.40	.45
Tannic, U. S. P., bbls....lb.	.83	.83	.70
Tartaric, cryst., U. S. P...lb.	*.36	*.36	*.32
Acetone, drums.............lb.	.22	.25	.21
Alcohol,denatured, complete. gal.	.43	.43	.45
Ethyl, 190 proof, bbls...gal.	4.75	4.75	4.70
Amyl Acetate.............. gal.	3.50	3.50	2.50
Camphor, Jap, refined, cases .lb.	.88	.88	.86
Carbon Bisulfide, c/1.........lb.	.06¾	.06¾	.06¾
Tetrachloride...........lb.	.10½	.10½	.10½
Chloroform, U. S. P., drums..lb.	.35	.35	.35
Creosote, U. S. P............lb.	.50	.50	.40
Cresol, U. S. P...............lb.	.25	.25	.25
Dextrin, corn ....100 lbs.	3.74	3.74	3.09
Imported Potato.........lb.	.09	.09	.09
Ether, U. S. P., 100 lbs.......lb.	.13	.13	.13
Formaldehyde, bbls..........lb.	.15	.15	.16
Glycerol, dynamite, drums...lb.	.16½	.16½	.16½
Methanol, pure, bbls........gal.	1.16	1.16	1.35
Methylene Blue, med........lb.	2.25	2.25	2.25
Petrolatum, light amber......lb.	.04½	.04½	.03¾
Pyridine ....gal.	2.75	2.75	2.75
Starch, corn, pow'd.....100 lbs.	3.07	3.07	2.47
Potato, Jap.............lb.	.05	.05	.06¾
Sago...................lb.	.04½	.04½	.03½



MEDICINAL CHEMICAL PRICES

Average Price of Twenty Representative Fine Chemicals

Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	June 1	June 15	Jan. 1923
Beeswax, pure, white.........lb.	.36	.36	.36
Castor Oil, No. 3.............lb.	.14½	.14½	.13
Ceresin, yellow...............lb.	.08½	.08½	.08½
Corn Oil, crude, tanks, mills...lb.	.09½	.09½	.09¾
Cottonseed Oil, crude, f. o. b. mill....................lb.	.09¾	.10	.09⅝
Linseed Oil, raw, lc/l........gal.	1.17	1.17	.87
Menhaden Oil, crude, mills...gal.	.50	.50	.53
Neat's-foot Oil, 20°..........lb.	.16½	.16¼	.18½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	6.15	6.15	6.25
Rosin Oil, first run..........gal.	.47	.47	.45
Shellac, T. N................lb.	.81	.81	.80
Sperm Oil, bleached winter, 38°....................gal.	.99	.99	1.03
Stearic Acid, double pressed...lb.	.14	.13½	.12½
Tallow Oil, acidless...........lb.	.10½	.10¼	.11½
Turpentine, spirits of........gal.	1.09	1.06	1.56

METALS

	June 1	June 15	Jan. 1923
Aluminium, No. 1, ingots.....lb.	.24½	.24½	.23
Antimony, ordinary......100 lbs.	7.25	7.25	6.75
Bismuth.....................lb.	2.75	2.75	2.75
Copper, electrolytic..........lb.	.15	.15⅛	.14¾
Lake...................lb.	.15⅛	.15¼	.14¾
Lead, N. Y..............100 lbs.	7.25	7.00	7.80
Nickel, electrolytic...........lb.	.25	.25	.36
Platinum, refined, soft........oz.	116.00	116.00	118.00
Quicksilver, flask......75 lbs. ea.	68.00	67.00	73.00
Silver, foreign...............oz.	.65½	.65	.63
Tin.........................lb.	.42	.42	.39
Tungsten Wolframite....per unit	8.50	8.50	7.50
Zinc, N. Y..............100 lbs.	6.75	6.50	8.25

FERTILIZER MATERIALS

	June 1	June 15	Jan. 1923
Ammonium Sulfate, expt.100 lbs.	3.50	3.50	3.90
Blood, dried, f. o. b. N. Y...unit	4.00	4.00	4.70
Bone, 3 and 50, ground, raw..ton	30.00	30.00	28.00
Calcium Cyanamide, unit of ammonia..................	2.25	2.25	2.25
Fish Scrap, dried, wks.......unit	4.00	4.00	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.25	3.25	3.00
Tennessee, 78–80%......ton	3.25	3.25	3.00
Potassium Muriate, 80%....unit	.68	.68	.68
Tankage, high-grade, f. o. b. Chicago...............unit	3.25 & .10	3.25 & .10	4.75 & .10

COAL-TAR CHEMICALS

Crudes

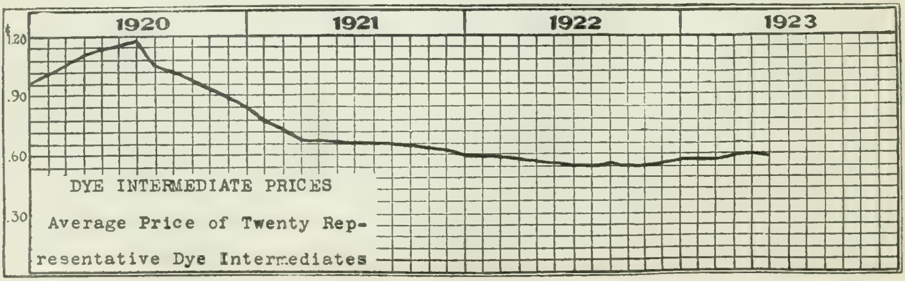
	June 1	June 15	Jan. 1923
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.27	.27	.30
Naphthalene, flake...........lb.	.08¼	.08	.06½
Phenol, drums...............lb.	.50	.50	.32

Crudes (*concluded*)

	June 1	June 15	Jan. 1923
Toluene, pure, tanks.........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, drums.................gal.	1.00	1.00	—

Intermediates

	June 1	June 15	Jan. 1923
Acids:			
Anthranilic..............lb.	.96	.96	1.10
Benzoic, tech............lb.	.70	.70	.65
Cleve's..................lb.	1.00	1.00	1.25
Gamma...................lb.	1.80	1.80	1.85
H........................lb.	.80	.80	.80
Metanilic................lb.	.60	.60	.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.62	.62	.60
Nevile & Winther's.......lb.	1.25	1.25	1.15
Picric...................lb.	.25	.25	.20
Sulfanilic................lb.	.20	.20	.19
Tobias'..................lb.	1.30	1.30	1.30
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil.................lb.	.17	.17	.17
Aniline Salt................lb.	.24	.24	.25
Anthraquinone (sublimed).....lb.	1.30	1.30	1.30
Benzaldehyde, tech...........lb.	.75	.75	.65
U. S. P.................lb.	1.50	1.50	1.40
Benzidine Base...............lb.	.84	.84	.84
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol...............lb.	3.80	3.80	3.75
Dianisidine..................lb.	4.60	4.60	4.50
p-Dichlorobenzene...........lb.	.17	.17	.17
Diethylaniline...............lb.	.60	.60	.60
Dimethylaniline..............lb.	.42	.42	.41
Dinitrobenzene..............lb.	.19½	.19½	.19
Dinitrotoluene...............lb.	.19	.19	.20
Diphenylamine..............lb.	.48	.48	.50
G Salt......................lb.	.55	.55	.60
Hydroquinol.................lb.	1.25	1.25	1.05
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist............lb.	.24	.24	.26
a-Naphthylamine............lb.	.35	.35	.29
b-Naphthylamine............lb.	.75	.75	.95
m-Nitroaniline..............lb.	.78	.78	.80
p-Nitroaniline..............lb.	.74	.74	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol...............lb.	1.00	1.00	.72
o-Nitrotoluene..............lb.	.10	.10	.10
p-Nitrotoluene..............lb.	.60	.60	.65
m-Phenylenediamine.........lb.	.98	.98	1.00
p-Phenylenediamine.........lb.	1.45	1.45	1.50
Phthalic Anhydride..........lb.	.32	.32	.35
R Salt.......................lb.	.55	.55	.55
Resorcinol, tech.............lb.	1.50	1.50	1.50
U. S. P.................lb.	2.00	2.00	2.00
Schaeffer's Salt..............lb.	.60	.60	.60
Sodium Naphthionate........lb.	.62	.62	.62
Thiocarbanilide..............lb.	.35	.28	.35
Tolidine (base)..............lb.	.95	.95	.95
Toluidine, mixed............lb.	.31	.31	.30
o-Toluidine.................lb.	.15	.15	.15
p-Toluidine.................lb.	.95	.95	1.00
m-Toluylenediamine.........lb.	.95	.95	.95
Xylidine....................lb.	.50	.50	.42



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EDITORIALS

Guide Posts

THE Tariff Commission has just issued the "Census of Dyes and Other Synthetic Organic Chemicals" for the calendar year 1922. Prepared under the direction of Warren N. Watson, the census is invaluable as a guide post to our manufacturers and enables specialization in production to be undertaken along the lines urged in our discussion last month. Indeed, earlier work of the commission has been of great monetary value to our industry because of its utility in just this manner. From the data given, plans can be laid that will greatly strengthen our world position.

There is much of encouragement in the census. For the first time in history, we are practically independent, producing now in this country 93.5 per cent of our requirements. In 1922, the dye production increased 66 per cent, imports decreased, and while exports also declined, they are now showing an increase. The gain in the production of vat and alizarin dyes is also most encouraging, and the decrease in imports is largely due to the successful commercial production during 1922 of these colors, as well as the developed cotton, acid, and mordant dyes.

Statistics speak clearly for themselves and the following are of great interest:

PRODUCTION OF SYNTHETIC ORGANIC CHEMICALS

	Number of Firms	Production in Pounds	
Coal-tar chemicals:	1922	1922	1921
Dyes	87	64,632,187	39,008,690
Color lakes	43	10,578,664	6,152,187
Photographic chemicals	7	345,798	183,798
Medicinals	..	2,946,347	1,545,917
Flavors	20	1,215,668	901,245
Perfumes	17	793,148	119,335
Synthetic phenolic resins	5	5,944,133	1,643,796
Synthetic tanning materials	4	1,910,519	1,902,597
TOTALS	164	88,368,131	51,457,565
Non-coal-tar chemicals	..	79,202,155	21,545,186

Those who have wondered to what extent the ultimate consumer may be subject to an American monopoly will be interested to know that there has been a decrease in the price of dyes, notwithstanding the unusually high cost of production in all lines of manufacture in the United States to-day. In 1917 the average sales price per pound of dyes was $1.26, in 1921, $0.83, and in 1922, $0.60. As compared with 1921 the price of indigo decreased 47 per cent and alizarin 20 per cent, with many other colors within the range. As to quality, we quote from the census:

> The satisfactory quality and the uniform standardization of the American dyes is one of the striking evidences of the commendable progress made by the industry. Dye for dye, with relatively few exceptions, the domestic products are found equal to the pre-war German dyes. In the early stages of the domestic dye industry, after the outbreak of the Great War, many of our dyes were lacking in uniformity of strength and quality. This condition, however, no longer prevails, as our domestic manufacturers are marketing dyes which are uniformly standardized as to strength and quality. Statements of the largest silk and woolen manufacturers and also from cotton printers and dyers agree as to the satisfactory results obtained from American dyes.

To be sure, many factors contribute to the success which thus far has rewarded the efforts of American scientists, industrialists, and capitalists to establish an industry here. Among these factors the unsettled situation in Europe, which cannot continue indefinitely, looms large. Most important is the item of research for which the coal-tar and chemical industry has expended, during the period 1917 to 1922, more than $21,000,000. Through this expenditure new dyes and other synthetic organic chemicals of great economic value have been devised and developed, while the reduction in prices, to which reference has been made, is in a large degree due to reduced cost of production, which is not possible without such research. There is perhaps no other American industry which has devoted such a sum to research and development work in the period named. This fact should do much toward allaying the fears of those who have been disturbed by what appears to have been a lack of appreciation of scientific men. In individual cases there has been, no doubt, such a disregard for the scientist as to give rise for anxiety; but industry as a whole does not seem to lack proper appreciation.

Just before the war we were discussing with an eminent European chemist the question of a dye industry in America. He predicted that America would not found such an industry—first, because it could not be done without the expenditure of at least ten million dollars upon research; and secondly, that the market was not worth that hazard. The record speaks for itself. There is still much to be done for the gap between 93.5 per cent and 100 per cent should be filled. That 6.5 per cent is obviously the most difficult. It requires the expenditure of large sums and the continued support of research on a large scale. All this can and will be done if the industry is given the support by the ultimate consumer which it has fully demonstrated is well deserved.

A Dangerous Precedent

THE sincere efforts on the part of such government departments as Agriculture and Commerce to obtain the best scientists possible for government service, and to make that service attractive to them, stand out in marked contrast to recent events in the Department of the Interior. The circumstances under which the director of the United States Reclamation Service has been deposed may easily establish a most dangerous precedent and cause good men needed in government service to decline to submit themselves to the possibility of similar action.

From information appearing in the public press, it seems that, for political reasons, an engineer with thirty-five years of satisfactory service to his credit has been dismissed, upon two weeks' notice, on the flimsy excuse that the service requires as its head a "business man" and not an engineer and that the new appointee will be able to assist the man on irrigated lands to make a success of his enterprise. It is not our purpose to comment upon the business experience of the new appointee, nor to express views as to the possible duplication of the work of the Department of Agriculture for the farmer, but rather to inquire if there are not now sufficient jobs for political distribution without disturbing engineering and scientific organizations. Technical men are little concerned with politics. That game has no attraction for most of those interested in scientific pursuits. Public welfare requires that the best qualified technical men obtainable be placed in government work. The compensation is inadequate in many instances, and the post must therefore be made as attractive as possible in other ways. Our politicians must be made to understand that technical work must be kept and placed beyond their reach.

Newspaper Education

No one minimizes the power of the daily press nor the opportunity which it has to educate a large portion of our population. It is this very function of the press which has made it worth while for the AMERICAN CHEMICAL SOCIETY to do what it could in supplying reliable information not easily obtainable by the press without such assistance.

Knowing something of the difficulty in interesting the press in scientific information, we have carefully noticed, from time to time, the relative amount of space given to news of various classifications chosen, undoubtedly, by the editor to meet what he believes to be the public demand. Can you recall any event connected with science or scientists which commanded even ten per cent of the space given to the recent prize fight in Shelby, Montana? One of the greatest newspapers in this country devoted one-half of its front page and at least two other pages in the same issue, not to mention an editorial, to this instructive and elevating event. This had been preceded by front page articles and was followed by further material which was also given preferred space. An international catastrophe, a declaration of war, or a presidental landslide is accorded a like amount of publicity.

Perhaps there is nothing discouraging in the situation but it does seem to indicate that much remains to be done before the press will be willing to devote space to events more nearly in proportion to their real and lasting importance. After all, it is a question whether the press really prints as news the topics in which the people are interested, or offers the class of news in which it seeks to interest the public.

Supplemental Meetings

The unqualified success of the Colloid Symposium at the University of Wisconsin, following close on the heels of the demonstration at the University of Illinois of how attractive a regional meeting can be made, clearly indicates that the report of the Committee on Intersectional Meetings should be given serious consideration at Milwaukee.

We find no general sentiment for discontinuing either of our semiannual meetings. The activities of the SOCIETY require that its governing body and its advisory and other committees should meet at least twice a year. Semiannual meetings also not only make it possible for a large number of members to attend at least one of our national meetings each year, but exert, both locally and nationally, an influence for chemistry which must not be underrated.

The growth of chemistry in America and the splendid work being done seems, however, to require the adoption of new policies governing meetings. First, the national meetings must be put upon a still higher plane. They must be made to assume a national importance and to attract the attention of a larger portion of our population. The number of papers before the divisions and sections must be reduced and only those papers presented which are of sufficient importance to draw forth discussion, for which ample time must be allowed. Such papers should be reviewed and edited before presentation so that they may be published without delay. The time now given to general meetings might be profitably divided with a symposium of general interest. Programs should be planned a long time in advance and given most serious thought.

This leaves the remainder of the papers, by far the larger part, for the regional meetings, and insures ample time for discussion, since such papers will be divided among a number of regional meetings. Whether these regional meetings should be modeled along national divisional lines or consist of symposia remains a question. Perhaps occasional symposia might also be held to advantage. That would, of course, depend largely upon the subjects to be discussed.

The impelling need of the moment seems to be to encourage the presentation of worth-while papers by creating such conditions that the authors of the best work will be encouraged to present their results. We should make sure that the cream of our effort is offered at the national meetings and in a setting and under circumstances which are attractive to the author as well as his audience.

Members should go to Milwaukee with definite ideas on this subject.

Chemists in High Places

In Rochester they tell the story that the Research Laboratory of the Eastman Kodak Company was founded by Mr. Eastman after a visit to Germany during which a prominent industrialist boasted of his own research staff and asked Mr. Eastman how many chemists he employed upon research.

C. E. K. Mees, who had been managing director of Wratten & Wainwright, of England, from 1906 to 1912, came to be director of the Research Laboratory in the latter year, and began to make his intimate acquaintance among American chemists at the meeting of the Eighth International Congress of Applied Chemistry. He has become prominent among American chemists, and notwithstanding his increasing duties with his company, has had time to contribute much to the success of the Rochester local section. We can commend such activity to the many other plant executives. The Superintendents' Club at Kodak Park can offer many an interesting story of the early experiences of Dr. Mees as one of their number.

Not long since there were added to the duties of directing research those incident to development, which carries with it the responsibility of investigating and advising new departures in manufacture, based either upon the company's own discoveries or suggestions from others. We are pleased to say that Dr. Mees has since been made a director of the Eastman Kodak Company, the election taking place at a recent meeting of the directors. This promotion is pleasing personally, and is of interest to all chemists, proving as it does that a man properly qualified and trained, and with a willingness really to work may succeed in reaching the highest places in a corporation by the chemical route. Having made a specialty of photographic theory and having a keen appreciation of scientific work both fundamental and applied, we venture the prediction that no director of the company will contribute more to the success of the corporation than Dr. Mees.

The election of chemists to high places in industrial organizations should not be so infrequent as to need editorial comment. The valuable qualities which the Eastman Kodak Company has discovered in Dr. Mees may be found by other commercial organizations among their own scientific staff. We venture to suggest that such an inquiry would reveal many men qualified to take such increased responsibility in the management of the company's affairs. Such a man will, of course, have native ability, made more valuable by the special training which a thorough grounding in chemistry and allied subjects is sure to give. With a little encouragement he will be able to pass sound judgment in differentiating between essentials and nonessentials in business, just as he must do in the course of his chemical work.

Recent Developments at Wilmington

THAT American industry is and must be protected from the exposure of industrial secrets in legal proceedings, was the substance of the most important ruling yet made by Judge Hugh K. Morris in the case of the United States vs. the Chemical Foundation, Inc., at Wilmington, Del. In the cross examination of Elmer K. Bolton, chief chemist for E. I. du Pont de Nemours & Company, it was evident that Colonel Anderson, attorney for the Government, must have been given information considered confidential by Dr. Bolton's employers. He asked direct questions as to the modifications of processes necessary to obtain the products claimed under patents which his company was using and answers would have disclosed valuable secrets. Following a heated controversy between counsel, the judge announced his ruling in these words:

> I decline to direct this witness to answer, and hold, for the first time in this case, that the testimony called for is irrelevant and immaterial and is not pertinent* * * *to this case.* * * *I decline to make public any answer or to place the trade secrets of any commercial enterprise, under the conditions here called for, either public or quasi-public property.

The importance of this ruling, which establishes a precedent against the rights of courts to force trade secrets into public records, cannot be overestimated.

Herman A. Metz testified, on direct examination, that the patents covering novocaine, arsphenamine, and neoarsphenamine were worth $1,200,000 to him and that he would have paid this amount for them at the time they were sold to the Chemical Foundation with the other German-owned patents for $250,000. On cross examination by the defense, Mr. Metz admitted that without exclusive rights to manufacture (a condition which was expressly forbidden the Foundation under its charter) the patents would have been worthless to him and he would not have placed a bid for them. The attorney for the defense, Isador J. Kresel, in his cross examination openly charged that Mr. Metz was the "invisible plaintiff," saying:

> The invisible plaintiff which we have claimed influenced government officials to bring this suit is no longer invisible. He is here, we shall show to the court, and we shall prove that this witness was not only the representative of the German dye and chemical interests but that he and the interests he is the agent for brought about this suit.

Former Alien Property Custodian A. Mitchell Palmer, the first witness for the defense, gave a dramatic account of the fight conducted by President Wilson, the Alien Property Custodian's Office, and the other agencies of the Government during the war to break up the hold Germany had on our industrial life, and of their efforts to insure to America a self-contained chemical industry through the formation of the Chemical Foundation. The findings of the Alien Property Custodian's Office showing the thorough way in which the Germans had insinuated themselves into all branches of our industrial life, the measures taken to combat them, and accounts of consultations with ex-President Wilson, in which he expressed a desire to rid America once and forever of this menace to our very life in times of war, all formed a part of Mr. Palmer's testimony.

The testimony of Francis P. Garvan, Mr. Palmer's successor as Alien Property Custodian, and president of the Chemical Foundation since its inception, like that of Mr. Palmer and Joseph H. Choate, Jr., tended to show the conditions under which the sale was made to the Foundation and the reasons of the administration for placing these patents in trust rather than selling them to individuals who might conceivably have established an American monopoly to replace the German monopoly. The purposes of the Foundation as outlined in its charter, its carrying out of these trusts, and accountings of its funds were introduced among the mass of evidence presented by these witnesses. Apparently, the object of these witnesses was to show that the entire transaction was carried out in good faith by the previous administration and that fraud was not involved, as claimed by the Government in its present suit.

The claim on which the Government bases its suit, that the $250,000 paid for the patents was absurdly inadequate, was combated by the defense in its subsequent testimony. The evidence presented by the experts called by the defense shows that the mere possession of patents did not constitute more than a fraction of the value of an actually working process. E. H. Volwiler, chief chemist of the Abbott Laboratories, testified that the patents under which his company was licensed to manufacture medicinals did not contain complete disclosures of the processes and that his firm had been forced to spend time and money in research to bring these processes into commercial operation. Among others, he testified that it had cost his company $35,000 in research to produce novocaine commercially. This evidence, as well as that subsequently introduced by the defense, supported the idea expressed by the counsel for the defense that the salient part of any process was the "know how." During this testimony the Government put in a plea to have the witnesses state in open court just what their researches have shown was necessary to make the products commercially. On this point, Judge Morris ruled that the court had no right to force a witness to reveal in open court the secrets on which his business depended, and that this testimony could only be taken under strictest conditions of secrecy in chambers.

Thomas W. Miller, present Alien Property Custodian, was introduced for cross examination by the defense, and his testimony supported the contention of the defense that if the patents were now returned to the Government they would probably be returned to their former German owners by Congress.

Julius Stieglitz, who acted as chairman of the Committee on Synthetic Drugs of the National Research Council and as adviser to the Federal Trade Commission and the United States Public Health Service during the war, was placed on the witness stand by the defense to contradict evidence presented by Herman A. Metz regarding the arsphenamine patents. He reviewed the work of the Public Health Service and the efforts which were made to make arsphenamine of such purity as to remove the possibility of a repetition of such deaths as were caused by its use during the war. This testimony and Mr. Metz's replies have been given wide publicity in the press.

Attention was then turned to the Haber patents.

Charles L. Parsons, former chief chemist of the Bureau of Mines, who went abroad as chemical engineer for the War Department to study the fixation of nitrogen in Europe, and a member of the Nitrate Commission during the war, testified that these patents did not contain the information necessary to work the processes but that extensive researches had been necessary to make them operate. His evidence was introduced to discredit the testimony of Karl Holdermann, of the Badische Company, that these patents were worth $17,000,000. Alfred H. White, formerly assistant chief of the Nitrate Division, and H. A. Curtis, formerly of the Nitrogen Fixation Laboratory, both testified to the same effect.

Throughout the trial Judge Morris maintained the attitude that the judiciary has no right to review the acts of the executives under the powers granted the President by the war-time acts of Congress. The attorneys involved have argued heatedly and frequently throughout the progress of the trial.

Effect of Dialysis on Direct Crystallization of Citric Acid from Lemon Juice[1]

By H. D. Poore

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Preliminary experiments using collodion sacs in dialyzing lemon juice, followed by dialysis on a large scale in an osmogene containing collodion-impregnated cloth membranes, gave the following results:

(1) The small quantity of colloids present in lemon juice does not affect crystallization, but the ash and other nonacid constituents prevent satisfactory crystallization of concentrated fermented juice.

(2) In the presence of ash and other impurities, needle and leaflet modifications of citric acid crystals are obtained; upon the removal of half of the ash, characteristic citric acid crystals are formed.

(3) At the concentration necessary for crystallization, the mother liquor is so viscous that the crystals cannot be separated.

In the commercial production of citric acid from lemons, the acid is precipitated from the clarified juice with calcium carbonate, and the calcium citrate formed is decomposed with sulfuric acid. The calcium sulfate is filtered off and the citric acid solution is concentrated and crystallized. Although only two major chemical reactions are involved in the process, a large number of operations necessitating careful supervision and laboratory control must be carried out in order to secure acid complying with the Pharmacopeia requirements.[2]

The average quantity of total acid present in a ton of lemons is 70 pounds. About 85 per cent, or 60 pounds, of this is obtained from the juice and maceration water. The final yield of crystallized acid varies from 40 to 45 pounds, showing a loss during the process of 15 pounds or more per ton of fruit.

Lemon juice has approximately the following composition: 6 per cent of total acid, nearly all of which is citric; 2 per cent of sugars, mostly invert; 0.3 per cent of protein; 0.4 per cent of ash; and 0.8 per cent of undetermined matter. The undetermined matter consists largely of gummy and pectic substances.

Peratoner and Scarlata[3] have devised a method of manufacture in which many of the nonacid constituents of the juice are precipitated by a mixture of alcohol and ether. At present, however, this process is not economically possible in the United States. It was thought that these impurities might be colloidal and that purification might be obtained through dialysis.

Determination of Colloids in Lemon Juice

A review of the literature on diffusion and separation of colloids from solution showed that the most satisfactory membranes were made of ether-alcohol collodion. A complete bibliography of their development is presented by Bigelow and Gemberling.[4] Many other investigators, including Brown,[5] Bechold,[6] Schoep,[7] Walpole,[8] Fouard,[9] and Eggerth,[10] have developed methods for producing graded series of membranes of definite permeabilities.

For the determination of the colloids in lemon juice, 500-cc. sacs that were impermeable to boiled starch, made from 4 per cent collodion solutions, were used. One hundred cubic centimeters of juice were added to each of two sacs, which were placed in distilled water held at 90° to 95° C. The water was changed every 3 or 4 hours during the daytime, and the dialysis was continued until the dialysate contained no acid. The contents of the sacs, which was colorless, was then removed and evaporated to dryness, and the total colloids were obtained. After ashing, the organic colloids were calculated. Duplicate determinations checked closely.

The effect of different methods of treatment and filtration upon the colloid content of lemon juice is shown by the results given in Table I.

Table I—Effect of Method of Treatment and Filtration on Colloidal Content of Lemon Juice

Lot No.	Kind of Juice	Treatment	Total Colloids %	Organic Colloids %
1	Fresh	Filtered through filter paper; still cloudy	0.078	0.072
2	Fresh	Same as No. 1; dialyzed at 25° C.	0.079	0.071
3	Fresh	Filtered repeatedly through asbestos until clear	0.039	0.036
4	Fresh	Filtered hot through paper with 2.8 per cent kieselguhr	0.033	0.030
5	Fresh	Filtered hot through paper with 2.8 per cent kieselguhr and 1.6 per cent kelpchar	0.022	0.021
6	Fermented, clear	....	0.036	0.034
7	Fermented, clear	Filtered hot through paper with 1.4 per cent kieselguhr	0.028	0.025
8	Fermented, clear	Filtered hot through paper with 2.8 per cent kieselguhr	0.027	0.024

The colloid content of the juice varied somewhat with the method of pressing the fruit, high pressures giving the greater quantity.

In order to determine whether it would be possible to separate part of the ash and sugars from the citric acid in lemon juice by fractional dialysis, the following experiment was conducted:

A sample of 250 grams of fresh lemon juice, containing 6.2 per cent of total acid, 2.1 per cent of total sugars, and 0.3 per cent of ash, was dialyzed. The dialysis was carried on in a beaker containing 700 grams of distilled water maintained at 80° to 90° C. At given intervals the dialysate in the beaker was weighed and 10 samples were removed for analysis. During the course of the experiment, which ran for 2.5 hours, water was added to the dialysate to replace that which evaporated. Table II shows the results of the analyses of the samples, the total quantities dialyzed, and the total percentage dialyzed. By plotting the percentages against the time, the curves in Fig. 1 are obtained. These show that the ash dialyzes more rapidly than the acid and sugar during the first hour, although the difference is not great enough to offer a means of removing part of the ash. As might be expected, the curves of the invert sugars and citric acid are practically the same.

Dialysis of Proteins

As the quantity of colloids found in the lemon juice was less than a third of that of the proteins, it seemed that most of the protein was not present in the colloidal state. Ost-

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[1] Received February 9, 1923.

[2] Wilson, This Journal, **13**, 554 (1921)

[3] Molinari, "Organic Chemistry," 2nd ed., part 1, p. 414.

[4] *J. Am. Chem. Soc.*, **29**, 1576 (1907)

[5] *Biochem. J.*, **9**, 594 (1915), **11**, 40 (1917

[6] *Z. physik. chem.*, **60**, 257 (1907), **64**, 328 (1908)

[7] *Kolloid-Z.*, **8**, 80 (1911).

[8] *Biochem. J.*, **9**, 284 (1915).

[9] *Bull. assoc. chim. sucr. dist.*, **28**, 756 (1911).

[10] *J. Biol. Chem.*, **48**, 203 (1921).

TABLE II—COMPARATIVE RATE OF DIALYSIS OF ACID, SUGARS, AND ASH OF LEMON JUICE

		Acid			Total Sugar as Invert			Ash		
Time Minutes	Weight of Dialysate G.	In Dialysate %	Removed for Samples G.	Dialyzed %	In Dialysate %	Removed for Samples G.	Dialyzed %	In Dialysate %	Removed for Samples G.	Dialyzed %
10	675	0.50	0.085	21.8	0.16	0.027	20.0	0.033	0.006	32.4
20	637[a]	0.80	0.22	33.4	0.29	0.076	35.6	0.043	0.013	40.7
30	698	1.00	0.39	46.5	0.33	0.13	43.9	0.053	0.022	55.7
45	653[a]	1.35	0.62	59.5	0.47	0.21	60.5	0.067	0.033	66.7
60	645[a]	1.55	0.88	68.5	0.51	0.30	66.8	0.068	0.045	68.6
90	640	1.70	1.17	75.9	0.58	0.40	76.1	0.070	0.057	71.7
120	575	1.90	1.50	78.0	0.64	0.51	77.0	0.080	0.070	75.1
150	555	1.95	....	79.5	0.67	.....	80.1	0.087	...	80.4

[a] 100 cc. of water were added to the dialysate at the end of 20 minutes, 50 cc. at the end of 45 minutes, and 50 cc. after 60 minutes.

wald[11] states that some proteins dialyze in acid solution, and the following experiment showed that this is true of the lemon protein:

Two collodion sacs were filled with 100 cc. of fermented concentrated juice containing 18.4 per cent of acid and 0.62 per cent of protein. The sacs were placed in 100 cc. of water, maintained at a temperature of 80° to 90° C. for 5 hours, and then left over night at room temperature. The dialysates were diluted to 100 cc. and analyzed, with the results shown in Table III.

TABLE III

	Dialysate			
Test No.	Acid %	Protein %	Acid Dialyzed %	Protein Dialyzed %
1	12.7	0.47	69	76
2	11.8	0.52	64	84

In order to determine the effect of temperature and agitation of the dialysate on the rate of dialysis of the acid, three tests were made. In each, 100 cc. of fresh lemon juice, containing 6.5 grams of total acid, were pipetted into a sac, which was then placed in 250 cc. of water. Samples of the dialysate were removed at intervals, and the total amount of acid dialyzed was determined. The results are shown in Table IV.

TABLE IV

		Acid Dialyzed for					
		30 Minutes		60 Minutes		120 Minutes	
Test No.	Temperature ° C.	G.	%	G.	%	G.	%
1	20		.	2.8	43	3.8	58
2	82	3.3	51	4.5	69	.	
3[a]	82	3.8	58	5.0	77	.	

[a] Agitated.

These results show that agitation increased the rate of dialysis at 82° C. about 12 per cent, and that 60 per cent more acid dialyzed in one hour at 82° C. than at 20° C.

The combined dialysates obtained in these experiments were evaporated to about 55 per cent acid. The thick sirup obtained did not crystallize, even after it was seeded with fine citric acid crystals and allowed to stand for several weeks.

In the next test 3 liters of fermented juice which contained only a trace of sugar were dialyzed. Concentrating the dialysate to 68 per cent acid gave a thick sirup, which crystallized after standing for a week. The liquor from these crystals, however, was so thick that it was only partially separated on a Büchner funnel. Upon attempting to wash with ice water, some of the crystals dissolved and only part of the adhering sirup was removed. After filtering with charcoal three recrystallizations were required before pure white crystals were obtained.

OSMOGENE AND MEMBRANE

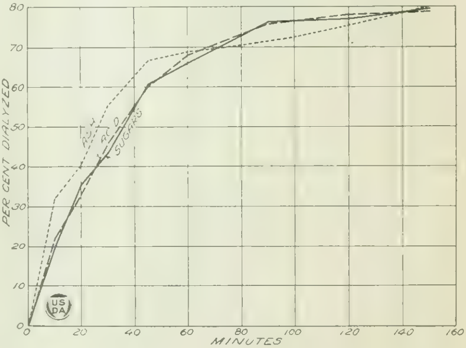
To facilitate work upon a larger scale, a small osmogene of 13 frames, 25 cm. square, was used. In order to save the lemon juice dialysate, a countercurrent arrangement, whereby the lemon juice passed through the even-numbered frames and the water or dialysate flowed in the opposite direction, through the odd-numbered frames, was adopted. In this manner, by regulating the flow and employing enough frames, the dialysate should leave the osmogene at the same acid strength as that of the juice entering. Both the juice and dialysate water were heated to about 90° C.

Although parchment paper has been used in the sugarhouse osmogenes, it was found, after testing the best grades obtainable, that the life of the paper was too short and that the speed of dialysis was much too slow. Walpole,[8] Brown,[5] Hatschek,[12] and others have experimented with sheet collodion and collodion-impregnated cloth and paper. Many methods of preparing membranes were tried in order to find one that would be satisfactory.

TABLE V—CONCENTRATED DIALYSATES

	Composition Per cent			Ratio of Final to Original Concentration			
Determination	Lot 1	Lot 2	Lot 3	Lot 1	Lot 2	Lot 3	Average
Acid	66.91	67.3	66.11	11.9	12.0	11.7	11.9
Ash	5.20	4.90	4.64	14.9	14.0	13.3	14.1
Sugars	1.05	1.13	1.15	13.1	14.1	14.4	13.9
Protein	2.31	2.06	2.25	12.1	10.8	11.8	11.6
Undetermined	10.91	10.07	9.92	12.8	11.8	11.7	12.1

The best membrane was obtained by moistening cambric or long cloth with alcohol, dipping it in 4 per cent collodion solution, and drying until it began to curl. The time of drying was 25 minutes at a room temperature of 18° C., 20 minutes at 23° C., and 15 minutes at 27° C. This membrane was impermeable to boiled potato starch when tested with lemon juice containing about 0.1 per cent of the starch and held at 85° C. The rate of acid dialysis through it was about 80 per cent of that of a collodion sac and double that of parchment paper. It will last several times as long as the parchment paper, the danger of breaking being eliminated.



DIALYSIS IN OSMOGENE

One hundred and fifty-five gallons of lemon juice were fermented until only 0.08 per cent of sugars remained, giving a product of the following composition:

	Per cent
Total solids	7.49
Total acid as citric	6.02
Fixed acid as citric	5.63
Total ash	0.35
Protein ($N \times 6.25$)	0.19
Invert sugar	0.08
Undetermined	0.85

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[11] "Handbook of Colloid Chemistry," p. 270.

[12] "Laboratory Manual of Elementary Colloid Chemistry," pp. 25 and 70.

TABLE VI—COMPOSITION OF CONCENTRATED LEMON JUICE BEFORE AND AFTER ALCOHOLIC PRECIPITATION

DETERMINATION	Lot 1		Lot 2		Lot 3a		Lot O_2	
	Before Per cent	After Per cent	Before Per cent	After Per cent	Before Per cent	After Per cent	Before Per cent	After Per cent
Total solids	86.4	81.7	85.4	81.5	84.7	81.4	84.9	83.8
Acid	66.9	64.0	67.3	62.2	68.2	67.6	63.0	66.9
Total sugars	1.05	0.86	1.13	0.75		1.00		1.14
Protein	2.31	1.81	2.06	1.83		1.63		2.19
Ash	5.20	1.80	4.90	2.30	4.89	1.66	5.34	2.35
Undetermined	10.9	13.2	10.1	14.4		9.5	...	11.2
Solids less acid	19.5	17.7	18.1	19.3	16.5	13.8	21.9	16.9
Per cent acid / Per cent solids	77.4	78.3	78.8	76.3	80.5	83.0	74.2	79.8
Per cent ash / Per cent acid	7.8	2.8	7.3	3.7	7.2	2.5	8.5	3.5

Three lots of this fermented juice were put through the osmogene.

Lot 1, consisting of 97 liters of unfiltered but nearly clear juice, was dialyzed for 84 hours, although the juice and water were actually in motion only 21 hours. Ninety-three liters of dialyzed juice having an acid content of 3.6 per cent and 132 liters of dialysate having 1.9 per cent acid were collected. While the fluids were in motion, a flow of approximately 6 liters per hour was necessary to maintain a temperature of 80° C. As the total area of the 12 membranes was but 0.75 square meter, four times this area would be required at the same rate of flow to yield a dialysate of 6 per cent acid. An osmogene of 50 frames, 90 cm. square, would deliver 75 liters per hour of dialysate of approximately the same acid strength. This dialysate was evaporated in a 40-gallon vacuum pan to 6 kg., filtered, and evaporated on a water bath, below 85° C., to approximately 67 per cent acid. It was then allowed to crystallize.

Lot 2 was put through in a similar way, except that the membranes used in the osmogene were dried for 5 minutes at room temperature. The dialysate was slightly turbid.

Lot 3, consisting of 82 liters of fermented juice which had been concentrated to 16.4 per cent acid content, was dialyzed. In order to check the evaporations made in the vacuum pan where unavoidable overheating occurred, 5 liters of this lot were evaporated directly on the water bath at 70° C. to 67 per cent acid content. This lot is designated in Table VI as *3a*.

CRYSTALLIZATION OF CONCENTRATES

Very small needle crystals with blunt ends appeared in two days in Lots 1, 2, and 3, and at the end of 10 days the thick viscous sirups were completely filled with the needle crystals. These crystals were not pointed, but had a columnar shape wholly unlike the characteristic citric acid crystals, which are rhombic prisms. The same difficulty was experienced in trying to separate the crystals as in the experiments on a laboratory scale. The concentrated liquors were so viscous that it was impossible to separate and wash them.

In order to determine whether crystals could be obtained from less concentrated liquors, samples were removed from Lots 1 and 2, and water was added to give concentrations of acid ranging from 52 to 62 per cent. After seeding and standing for 6 weeks, the more highly concentrated samples were filled with crystals, about half needle-shaped and half rhombic prisms. The other samples contained a few crystals, some characteristic types, but largely needle-shaped. Evaporation had taken place until 65 per cent of acid was present. These results show that large quantities of crystals will not form below a 65 per cent concentration, and that this concentration is too great to permit separation of the crystals from the heavy sirup produced.

After 13 days, Lot *3a* was filled with very small rhombic prisms, the mother liquor containing 65 per cent acid. The crystals were dissolved in a little water and allowed to recrystallize. The crystals formed were neither rhombic prisms nor needles, but were of an irregular shape resembling leaflets. Upon a second crystallization, needle crystals were formed. When some of the mother liquor from the leaflets was touched on the microscopic slide, fine needle crystals were formed. After a third crystallization, about two-thirds needles and one-third characteristic citric acid crystals were present. Leaflet crystals were formed on the fourth crystallization, and on the fifth crystallization rhombic prisms, with a few needles. Because of the minuteness of the crystals and their intimate mixture with the sirup, attempts to separate them on the microscopic slide and to identify them chemically were unsuccessful. Considering the large quantities formed each time, there is little doubt, however, that both the needle and leaflet crystals are citric acid. These modifications probably are produced by the large proportions of ash, protein, and undetermined matter present.

CRYSTALLIZATION OF CLARIFIED JUICE

In order to determine whether fermented juice treated with kieselguhr would crystallize as well as or better than the dialyzed juice, three lots (O_1, O_2, and O_3) containing 19.2 per cent of acid, were treated with kieselguhr, evaporated, and allowed to crystallize. Results similar to those obtained with Lots 1, 2, and 3 were secured. Needle, leaflet, and rhombic crystals were again produced. Upon seeding these samples with citric acid crystals, growths of needle crystals started on the seeding crystals and developed in size until they were as large and of the same shape as the needle crystals previously formed.

RECRYSTALLIZATION AFTER REMOVAL OF ALCOHOL PRECIPITATE

Samples of about 30 grams removed from Lots 1, 2, *3a*, and O_2 were made to 200 cc. with 95 per cent alcohol, and the heavy precipitate was filtered off. The filtrate was evaporated to a sirupy consistency, 100 cc. of water were added, and the solution was evaporated to about 65 per cent acid. After cooling, the material was seeded with citric acid crystals. At the end of 8 days, Lots 1 and 2 were filled and Lots *3a* and O_2 were partially filled with crystals. No needle or leaflet crystals were present. All were highly viscous, so that it was impossible to separate the crystals. Table VI shows the analyses of these lots before and after alcoholic precipitation.

The results show that more than half of the ash and small quantities of the sugars, protein, and acid were removed by the treatment. The proportion of ash to acid was lowered from an average of 7.7 to 3.2 per cent. The excessive amount of ash present before alcoholic treatment with the other nonacid constituents probably produced the needle and leaflet crystals. The process of Peratoner and Scarlata[3] doubtless removes a large proportion of the ash. These results also agree with those obtained in the dialysis of molasses where the excessive amount of salts prevents crystallization of cane sugar.

Commercial Acid Liquors

In order to compare the composition of the citric acid liquors obtained in this investigation with that of the concentrated mother liquors produced in citric acid factories, two samples taken from lead crystallizing pans were analyzed. Sample 1 came from a pan containing liquor that had been reworked four times. This means that the mother liquor had been removed from a batch of crystals, mixed with some fresh acid liquor, reduced to 38° Baumé, and allowed to crystallize. This was repeated four times, so that Sample 1 contains an accumulation of salts, sulfuric acid, and other impurities from five lots of acid liquor. Sample 2 had been reboiled three times. After liquors have been reworked more than three or four times, they yield such poor crops of crystals that it is customary to return them to the neutralizing tanks and recover the acid as citrate of lime. The composition of these samples was as follows:

	Sample 1 %	Sample 2 %
Total solids	74.09	72.48
Ash	3.01	4.08
Total acid as citric	67.81	65.29
Undetermined	3.27	3.11

A determination of total sulfates indicated that about 3 per cent of the total acid was sulfuric. These results show that, for approximately the same acid content, the dialyzed liquors (Table V) contain over 10 per cent more of total solids than the factory liquors made by the decomposition of calcium citrate with sulfuric acid. The factory liquors had such a low viscosity that the crystals could be readily removed and washed. The quantity of ash present, together with the small quantities of other constituents, is not great enough to prevent crystallization.

Acknowledgment

The author wishes to express his appreciation of the valuable assistance of E. M. Chace, chemist in charge, Laboratory of Fruit and Vegetable Chemistry, under whose supervision the work was conducted.

The Relation of Alcohol Precipitate to Jellying Power of Citrus Pectin Extracts[1]

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The amount of alcohol precipitate is not a reliable measure of effective pectin, as shown by comparisons of pectin solutions prepared in the open kettles and in an autoclave.

Determinations based upon jellying power give the only satisfactory means of estimating effective pectin content at present known to us.

Citrus pectin extracts prepared in an autoclave at 5 pounds pressure for 30 minutes had 25 per cent less jellying power than similar extracts prepared in the open kettle.

The addition of acid in open-kettle extractions of orange peel produced an extract of about 100 per cent greater jellying power than when no acid was used.

In order to ascertain whether a relationship could be established between the pectin content, as determined by the usual alcohol precipitation method, and the jellying power, a study has been made of a large number of pectin extracts prepared from the white peel of citrus fruits.

The work has involved the consideration of such details as the preparation of the peel, the proportion of water to peel, the number of extractions, the methods of filtration, concentration, and storage of the extracts, and their use in combination with different fruits and fruit juices in the making of jams and jellies. The results have shown that it is possible to prepare fairly concentrated pectin solutions from citrus peel, which can be used for making clear, transparent jellies without subjecting the extracts to a process of purification.

The investigation has been confined to a study of pectin solutions prepared in the open kettle and in the autoclave, with and without the addition of acid.

Extraction

The method of procedure adopted in this series of experiments for open-kettle cooking, was as follows: 226.7 grams of ground, white peel of oranges were extracted three times, using a liter of distilled water for each extraction. The heating was carried on in shallow pans of such a size that a concentration to about one-half the original volume could be accomplished in less than 20 minutes. The material was filtered through cloth. The combined filtrates amounted to 600 grams.

Extracting in the autoclave required considerable study before a procedure was adopted which gave solutions that were considered comparable with those prepared in the open kettle.

If pectins are unstable at the temperature of boiling water, it seems reasonable to suppose that they would be less stable at higher temperatures. However, if the heating period could be shortened, something might be gained by extracting in an autoclave. This idea seemed to be substantiated by the fact that autoclave extracts always gave a higher weight of alcohol precipitate than similar ones prepared in the open kettle.

By reducing the proportion of water and opening the petcock during cooling, it was possible to effect a concentration on the pomace equal to that obtained in the open-kettle process. Three extractions were made in every case, using 330 cc. of water to 226.7 grams of peel. The combined filtrates amounted to 600 grams. Extractions were made with pressures varying from 3 to 20 pounds and heating periods ranging from 10 to 40 minutes. Although there are several references in the literature to the use of the autoclave in making pectin extracts, which suggest its use as a means of increasing pectin yield, yet in no case has it been possible to prepare by this method a pectin solution which had as great jellying power as comparable extracts obtained by open-kettle heating.

Fellenberg[2] called attention to the fact that protopectin changes to pectin more rapidly in acid than in neutral solution. The writers had observed that lemon peel, which has a natural total acidity two to four times greater than that of orange peel, is always much more completely disintegrated at the end of the extraction process. In view of Fellenberg's statement, it seemed that the more thorough breaking up of the tissue might be due to the greater acidity of the lemon peel. With this idea in mind, a series of experiments was conducted similar to the ones just described, with the exception that 0.1 *N* citric acid was used instead of distilled water.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923, under the title, "Experimental Studies of Citrus Pectin Gels."

[2] *Biochem. Z.*, **85**, 118 (1918).

Comparisons of the extracts prepared by these different methods were based upon results obtained with the same lot of citrus fruit. This precaution was necessary since the pectin content varies within wide limits depending upon the variety and maturity of the fruit.

Determination of Pectin Content

The pectin content of these extracts was determined directly by the alcohol precipitation method and indirectly by measuring their jellying power or the amount of extract required to form a jelly with a definite weight of sugar and acid.

Neither of these methods, as at present applied, can be regarded as entirely satisfactory. The alcohol precipitation method gives widely differing results with the same extract, depending upon variations in manipulation. Alcohol also precipitates substances other than pectin, such as vegetable gums and hemicelluloses. The Campbell alcohol method gives consistently higher results than the method adopted in these experiments, which involves two precipitations.

Estimations of pectin content based upon jellying power are subject to error because of the lack of a definition of what constitutes a jelly and of a standard method of measuring gel strength. In making use of this method an arbitrary standard had to be selected for the sake of comparison, as has been done by other investigators. The details of the process were as follows: A series of four to six jellies was made with each pectin solution, using 84 grams of sugar, amounts of pectin extract ranging from 20 to 80 gram, enough 1 *N* citric acid to bring the total acidity to 1.3 grams, and enough distilled water to bring the volume to 150 cc. The mixture was then concentrated by boiling to 104° C., weighed, and poured into molds 1.25 inches deep and 2.75 inches in diameter. The weight of jelly at the concentration of 104° C. was usually 140 ±0.5 grams. The jellies therefore contained 60 per cent sugar and 0.9 per cent total acidity. The molds were loosely covered and allowed to stand 24 hours at room temperature before being turned out.

The standard gel was one barely stiff enough to retain its shape when removed from the mold, and it gave no immediate evidence of syneresis. The member of each series which corresponded to this standard was selected, and the amount of pectin extract which had been used in this jelly was taken as a measure of jellying power of the extract.

TABLE I—RESULTS WITH ORANGE PECTIN EXTRACTS PREPARED IN OPEN KETTLE AND AUTOCLAVE

Serial No.	METHOD	Alcohol Precipitate in Extract %	Acid in Extract (Calcd as Citric) %	Sugar in Jelly G.	Extract Used in Making Jelly G.	Grams of Jelly per Gram of Extract	Grams of Jelly per Gram of Peel
150	Open kettle Distilled water	0.347	0.07	84	70	2.0	5.2
151	Open kettle 0.1 *N* acid	0.890	1.90	84	27	5.2	13.7
154	Autoclave 5 lbs. 30 min. Distilled water	0.565	0.057	84	90	1.5	3.9
155	Autoclave 5 lbs. 30 min. 0.1 *N* acid	0.960	1.270	84	60	2.3	6.0
152	Autoclave 20 lbs., 30 min. Distilled water	1.690	0.120	84	90	No jelly	...
153	Autoclave 20 lbs., 30 min. 0.1 *N* acid	1.770	1.52	84	70	No jelly	...

Table I gives the results obtained in one series of experiments with orange pectin extracts.

A comparison of the figures in Columns 3 and 7 shows the disagreement between the quantity of alcohol precipitate and jellying power. Heating in the autoclave increases the amount of soluble matter in the extracts, yet when subjected to a jellying test these extracts prove to be quite deficient in jellying properties. Extracts in other series prepared at 10 and 15 pounds pressure for the same and shorter periods of time were similar in jelly-making strength to Nos. 152 and 153.

Doubtless, the instability of the pectin bodies at the high temperatures in the autoclave accounts for these results. It seems likely that the alcohol precipitate in this case consists chiefly of partially decomposed pectins, pectic acid, and possibly some hemicelluloses, which do not contribute to the jellying properties. The temperature reached in the ordinary process of making jelly from the pectin extracts (104° C.) seemed to bring about practically no destruction of pectin. Determinations of alcohol precipitate in jellies made according to the formula previously mentioned, agreed very closely with the value calculated from the amount of pectin extract used.

Effect of Acid

The favorable effect of acid in extracting orange pectin is shown in Table II, which gives results of two series of experiments.

TABLE II—RESULTS WITH TWO TYPICAL ORANGE PECTIN EXTRACTS PREPARED WITH AND WITHOUT ACID

Serial No.	METHOD	Alcohol Precipitate in Extract %	Acid in Extract (Calcd. as Citric) %	Sugar in Jelly G	Extract Used in Making Jelly G	Grams of Jelly per Gram of Extract	Grams of Jelly per Gram of Peel
125	Open kettle Distilled water	0.82	0.09	84	40	3.50	9.2
138	Open kettle Distilled water	0.79	0.085	84	40	3.48	9.1
124	Open kettle 0.1 *N* acid	1.30	1.70	84	20	7.0	18.0
139	Open kettle 0.1 *N* acid	1.24	1.24	84	20	7.0	18.0

It will be observed that in these extracts prepared with acid, increase in alcohol precipitate is accompanied by increasing jellying power, although not exactly in the same proportion. The fact that the acid extracts have 100 per cent greater jellying power whereas the alcohol precipitate shows an increase of only about 75 per cent over the distilled water extracts, seems to indicate that in the presence of acid not only is a larger quantity of pectin produced, but likewise a more effective pectin as regards jellying power.

The effect of acid on lemon peel extracts is not so marked, probably because of the greater natural acidity of the lemon. Lemon extracts in general contained a smaller percentage of alcohol precipitates; yet, their jellying power averaged about 20 per cent higher than that of the average orange peel extracts. This seems to be due to a difference in kind rather than in amount of pectin present.

Other Factors Influencing Jellying Power

To what extent the jellying property of these pectin extracts is affected by the foreign matter present, it is impossible to say. Pectin, as determined by the method used in these experiments, represents a very small percentage of the total solids extracted, and it is not unlikely that the other substances present may affect the character of the gel.

It seems very probable also, in view of the recent work of Tarr,[3] that the apparent variations in jellying power may be due in part to differences in the hydrogen-ion concentrations of the gels. Even though the total acidity was kept at a constant value, there may have been considerable difference in hydrogen-ion concentration due to the buffer effect of other substances in solution.

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[3] Delaware Agr. Expt. Sta., *Tech. Bull.* **134**.

Fellenberg[2] mentions the fact that the viscosity of pectins decreases with decreasing methoxyl content. In this connection it may be of interest to note that the acid pectin extracts of high jellying power had greater viscosity than did autoclave extracts in which the jellying properties were greatly reduced.

CONCLUSION

The true explanation for the discrepancies which have been pointed out involves a knowledge of the pectin bodies both as regards their constitution and their colloidal nature, which at present is not available.

As a result of unfinished tests with purified pectins, the writers concluded that quantitative relations in sugar-pectin-acid gels cannot be correctly interpreted, nor can any great advance be made in the study of the colloidal properties of these solutions until there are available for careful experimentation pectins of a high degree of purity and of well-defined composition.

When the relation of jellying power to composition is once established, a very satisfactory method of estimating effective pectin content, based upon jellying power, can be developed. Such a method, to be capable of general application, will require an accurate device for measuring gel strength under carefully standardized conditions.

Jellying of Sorghum Sirup[1]

Effect of Malt Diastase upon the Filtration of Sorghum Juice

By Sidney F. Sherwood

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Starch seems to be largely responsible for the jellying of sorghum sirup and for the extreme difficulty in filtering sorghum juice, especially after it has been heated. Preliminary treatment of the juice with malt diastase greatly increases the rate of filtration and prevents the "jellying" of the finished sirup.

THE cause of jellying of sorghum sirup, a characteristic well known to manufacturers, has not yet been explained. Although much of the sirup produced seems to have no jellying characteristics, jellying may occur at any time, ordinarily becoming manifest either immediately after the finished sirup has become cold or after the cold sirup has been stored for some time. Jellied sirup varies from a slightly slimy material to a gelatinous semisolid resembling ordinary table jelly prepared from fruit juices. Sirup of this character is highly unsatisfactory to both the dealer and the consumer.

Many of the sirups made from different varieties of sweet sorghum in connection with some breeding experiments and varietal tests on sweet sorghums conducted by this laboratory (project in charge of H. B. Cowgill, agronomist, under the direction of C. O. Townsend, pathologist in charge of office), had a jelly-like consistency. The starch content of 15 samples of juice expressed from 15 varieties of sorghum at maturity varied from 0.142 per cent (1.3 pounds per 100 gallon of juice) to 0.852 per cent (7.8 pounds per 100 gallon), with an average of 0.366 per cent (3.3 pounds per 100 gallon).[2] Starch seems to be largely responsible for the jellying propensity and for the extreme difficulty hitherto experienced in filtering sorghum juice, especially after it has been heated. Apparently, preliminary treatment of the juice with small quantities of malt diastase greatly increases the rate of filtration and prevents jellying.

EXPERIMENTAL

Freshly ground malt was mixed with water in the proportion of 25 grams to 200 cc., stirred frequently during 1 hour, and filtered through filter paper. The resulting extract was perfectly clear. A Büchner funnel, 6 inches in diameter, was fitted with a single thickness of closely woven cotton cloth, which was then faced with a layer of kieselguhr approximately 2 mm. thick. The juice was kept thoroughly stirred while being poured on the filter, so as to build up an even cake, and vacuum was maintained at a closely constant rate for all runs.

The following sirups were prepared from juice from Silver Top, Folger's Early, Sugar Drip, Early Rose, Early Amber, and Red Amber sorghum, grown at Arlington Farm, Va., in 1922. The quantity of starch in the juice was not determined, but all the juices gave a positive reaction with iodine, and when preserved with mercuric chloride and allowed to settle exhibited in the settlings a starch layer or band. The tables are based upon nine series of determinations and the results are in entire agreement with similar investigations made in previous seasons.

SIRUP A—Approximately 900 cc. of juice plus 1 ounce of kieselguhr (3 per cent by weight), heated to 98° C., and filtered at once.

SIRUP B—Approximately 900 cc. of juice plus 1 ounce of kieselguhr, stirred, and filtered at once without heating.

SIRUP C—Approximately 900 cc. of juice heated to 98° C., cooled to 40° C., 10 cc. of malt extract added, permitted to stand for 1 hour, 1 ounce of kieselguhr added, and filtered at once.

SIRUP D—Approximately 900 cc. of juice heated to 98° C., cooled to 40° C., 10 cc. of malt extract added, permitted to stand for 1 hour, 1 ounce of kieselguhr added, heated to 98° C., and filtered at once.

SIRUP E—Identical with Sirup D, except that 20 cc. of malt extract was used.

The rate of filtration of these juices is shown in Fig. 1.

The effect of the diastase upon starch in the juice was investigated further by adding ordinary cornstarch to juice obtained from Early Rose and Red Amber sorghum. Starch was added at the rate of 15 grams per gallon (3.3 pounds per 100 gallon), the average of the figures given for starch content of normal sorghum juice. Some of this juice was treated with kieselguhr and with malt extract in the following proportions:

SIRUP F—Approximately 900 cc. of juice, heated to 98° C., cooled to 40° C., permitted to stand for 1 hour, 1 ounce of kieselguhr added (3 per cent by weight), heated to 98° C., and filtered at once.

SIRUP G—Approximately 900 cc. of juice, heated to 98° C., cooled to 40° C., 20 cc. of malt extract added, permitted to stand for 1 hour, 1 ounce of kieselguhr added, heated to 98° C., and filtered at once.

The rate of filtration of these juices is shown in Fig. 2.

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[1] Received March 3, 1923.

[2] THIS JOURNAL, 15, 727 (1923).

The remarkable effect of treatment with malt extract upon the rate of filtration of sorghum juice is shown in Figs. 1 and 2. Direct filtration of unheated juice to which kieselguhr had been added gave an average of 285 cc. filtrate in 2 minutes, and 515 cc. in 5 minutes. The heated juice gave an average of 90 cc. of filtrate in 5 minutes. In both cases filtration practically stopped after 5 minutes. It may be said that the heated juice refused to filter. Juice that had been treated with malt diastase filtered readily, giving an average of 800 cc. of filtrate in less than 2 minutes. The filtration continued at a satisfactory rate. Treating ordinary sorghum juice with malt extract is as satisfactory at the rate of 10 cc. of extract to 900 cc. of juice (equivalent to approximately 1 gallon of extract to 100 gallons of juice) as at the rate of 20 cc. to 900 cc. (Juices D and E.) When starch was added, the untreated juice refused to filter (Fig. 2). The treated juice filtered readily (average of 800 cc. of filtrate in 2 minutes) and continued to filter beyond 12 minutes although at a slower rate. At the end of 12 minutes the filter cake was 3/4 inch thick. In every case, whether or not the juice had been treated with malt extract, the filtrates had a light amber color and were perfectly clear and brilliant.

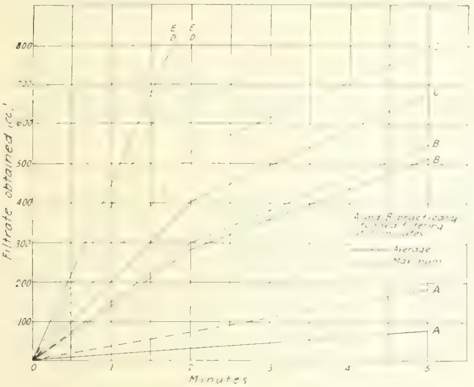

Fig. 1

Effect of Treatment on Sirup

All the experimental sirups were made by direct open-pan evaporation of the filtrates. Control or check samples were prepared from portions of the original raw juice. The process followed was similar to the one ordinarily used in the commercial production of sorghum sirup—a simple, direct, open-pan evaporation by rapid boiling, without the use of clarifiers or filtration, and removal of scums by simple skimming. The raw juice gave the usual copious quantities of green and yellowish scums. A particularly noteworthy characteristic of the boiling of the filtrates was that no scums were formed. When the sirup had become very dense, the usual small quantity of foam characteristics of the boiling of any high-density sugar sirup was evolved. The treatment resulted in the entire removal of the scum-forming constituents of the juice.

It is unnecessary to give in detail the characteristics of the sirups prepared. None of those from the raw juice were perfectly clear, and most of them were cloudy and contained specks and particles of suspended material. The color varied from light to very dark amber. Some were smooth and free flowing, while others had a marked slimy or gelatinous consistency. Those prepared directly from raw juice containing added starch were extremely gelatinous and contained transparent, gummy, lumpy masses.

The sirups prepared from the filtrates from the treated juice presented a marked contrast to those from the raw juice. All were smooth and free flowing; none were slimy or gelatinous. This was true also of the sirup from the juice containing added starch, although one such sirup contained a few minute, transparent, gummy particles. It is probable that the starch in the original juice plus that added made such a large total that either the malt extract or the period of time was insufficient for its complete conversion. None of the sirups showed indications of jellying or sliminess after 4 months storage at room temperature. The color of the sirup was practically identical with that of the sirups from corresponding original raw juice. Several of them were perfectly clear but most of them were slightly cloudy. The degree of cloudiness, however, was markedly less than that of the corresponding sirup from original raw juice, and no particles of suspended material appeared. The clouding did not take place until the liquid had been reduced nearly to finished sirup. Probably it was due to the decomposition of certain constituents at the higher temperature that prevails in boiling the thick sirup. Possibly this cloudiness could be avoided by a lime clarification immediately after treatment with the malt extract or by filtration of the nearly finished sirups. The investigation was directed particularly to the jellying, however, and this point was not investigated.

There was no appreciable difference in taste or flavor of sirup from treated and untreated juice.

Sucrose and reducing sugars calculated to a water-free basis, determined in several sirups, are reported in Table I.

Table I—Composition of Sirup on Water-Free Basis

Sample[a]	Sucrose (Clerget) %	Reducing Sugars (as Invert Sugar) %	Total Sugars (Sucrose plus Invert) %
1 *R*	60.61	24.99	85.60
1 *M*	61.96	25.23	87.19
2 *R*	60.85	24.89	85.74
2 *M*	25.21	60.09	85.30
3 *R*	72.47	17.20	89.67
3 *M*	42.79	46.54	89.33
4 *R*	66.17	21.96	88.13
4 *M*	66.26	22.88	89.14
Average *R*	. .	. .	87.29
M	. .	. .	87.74

[a] *R*, sirup direct from original raw juice; *M*, sirup from treated and filtered juice.

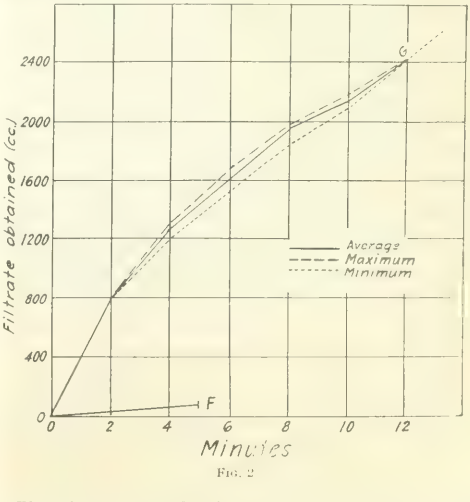

Fig. 2

There is no appreciable difference in the amount of total sugars in the sirup. No explanation is offered for the marked inversion that occurred in the case of Samples 2 and 3, although it may have been due to the effect of natural acidity of the juice. It is highly advantageous from the standpoint of sirup production, because the presence of invert sugar retards, and when present in sufficient quantity, prevents crystallization of sucrose.

For purposes of sirup production, it would seem to be desirable to select or breed varieties of sorghum, the juice from which contains minimum quantities of starch at maturity. However, the ease of filtration of the juice, the elimination of jellying of the sirup resulting from treatment with malt diastase, and the elimination of scum-forming constituents by filtration, indicate that the process may be applied with great advantage to the commercial production of sorghum sirup.

Suitability of Various Solvents for Extracting Vanilla Beans[1]

Part I

By **J. B. Wilson** and **J. W. Sale**

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Because of the restrictions on the use of alcohol which have followed prohibition, and the consequent substitution of other solvents for extraction of flavors, some preliminary work has been done to determine whether or not these alcohol substitutes produce the same amount and kind of extracts as those prepared from ethyl alcohol. This investigation was limited to several varieties of vanilla and the tonka beans, and the solvents selected were isopropyl alcohol, ether, acetone, and carbon tetrachloride, to be compared with ethyl alcohol. The results show that the alcoholic solvents are much superior from the standpoint of quantity of extraction, the carbon tetrachloride being the poorest in this respect. It is possible, however, that a preliminary extraction with ether or carbon tetrachloride followed by a weak alcoholic solution may be found practicable. Work on the analysis of the final extracts is still in progress.

With the advent of prohibition and the consequent placing of restrictions on the purchase and use of alcohol, considerable interest has been manifested in the suitability of solvents other than ethyl alcohol for the manufacture of oleoresins and flavors, and also in the reduction of the quantity of ethyl alcohol which is used. The United States Department of Agriculture, in *Circular* **136**, defines a flavoring extract as "a solution in ethyl alcohol of proper strength of the sapid and odorous principles derived from an aromatic plant, or parts of the plant, with or without its coloring matter, and conforms in name to the plant used in its preparation." It is further held, under the Federal Food and Drugs Act,[2] that "nonalcoholic flavoring products may be labeled with the term 'flavor,' provided they contain the same kinds and proportions of flavoring ingredients as are required by the Department's definitions and standards for extracts," and provided they comply with certain other requirements. Therefore, when oleoresins or flavors are prepared with solvents other than ethyl alcohol of proper strength, the question immediately arises as to whether or not the oleoresin or the finished flavor has "the same kinds and proportions of ingredients" as the oleoresins and flavoring extracts prepared with ethyl alcohol of proper strength. It is obvious that considerable information on this question can be obtained by the analysis of extracts and flavors made by extracting beans, roots, etc., with various solvents. Laboratory work along this line covering vanilla and tonka beans was started in the fall of 1922, and there are submitted herewith some preliminary data which are being supplemented by further laboratory work. The important question of the toxicity of the solvents was outside the scope of this investigation.

General Procedure

A quantity of Mexican, Bourbon, and Tahiti vanilla beans and of tonka beans was secured from a reliable importing house, cut to about $^1/_4$ inch in length with scissors, placed in a wooden bowl, and more finely divided by means of a meat chopper. One hundred-gram portions were placed in 500-cc. Erlenmeyer flasks and covered with 200 cc. of solvent. The solvents used were 65 and 95 per cent ethyl alcohol, isopropyl alcohol, ether, acetone, and carbon tetrachloride. In one series of operations the beans were mixed with 6 grams of potassium carbonate and then extracted with 65 per cent ethyl alcohol.

The analytical characters of vanilla extracts made with 65 and 95 per cent ethyl alcohol and with alkaline 65 per cent ethyl alcohol are quite well known, so that these solvents were used as standards with which to compare the characters of the extractive matters obtained with the other solvents. Isopropyl alcohol, ether, acetone, and carbon tetrachloride were selected, because they are available in large quantities and have sufficiently low boiling points so that they can be removed from the extracted matters at a low temperature under reduced pressure without affecting the quality of the oleoresins. Moreover, their cost is reasonable when it is considered that they can be recovered and used over and over again. The flasks containing the beans and solvents were closed with rubber stoppers and covered with tinfoil. The finely cut beans were macerated in the solvents for five days or more with frequent mixing, and then separated from the supernatant liquids by decantation, placed in a percolator, and drained, fresh solvent being poured over the beans to make the volume of the extract up to 200 cc. Two additional portions of 25 cc. each of fresh solvent were used to wash the beans. A second extraction was conducted in a similar manner except that the solvents were kept in contact with the beans for 4 weeks or more. There were thus obtained forty-eight solutions. The solvents were removed from all the solutions obtained from the two extractions, except those containing 65 per cent alcohol, at a temperature of not over 70° C., and a pressure of 100 to 25 mm. The quantities of extractive matter obtained are set forth in Table I. The various vanilla beans which had been practically exhausted with 95 per cent ethyl alcohol, isopropyl alcohol, ether, acetone, and carbon tetrachloride, were dried in the air and then subjected to the solvent action of 95 per cent ethyl alcohol for 2 weeks and the quantity of extractive matter determined after removal of the solvent at the temperature and pressure noted above. These results are set forth also in Table I. The tonka beans, which had been practically exhausted with the solvents just enum-

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[1] Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Service and Regulatory Announcement, Chemistry, **28**, Item 391.

Table I Total Extractive Matter in Vanilla and Tonka Beans, in Per cent
(Based on weight of beans)

Solvents	Mexican Vanilla				Bourbon Vanilla				Tahiti Vanilla				Tonka			
	1st Extraction	2nd Extraction	Sum of 1st and 2nd Extractions	3rd Extraction	1st Extraction	2nd Extraction	Sum of 1st and 2nd Extractions	3rd[a] Extraction	1st Extraction	2nd Extraction	Sum of 1st and 2nd Extractions	3rd[b] Extraction	1st Extraction	2nd Extraction	Sum of 1st and 2nd Extractions	3rd Extraction
Ethyl alcohol, 95 per cent	13.9	4.5	18.4	2.1	23.7	6.6	30.3	2.6	17.4	4.3	21.7	1.6	11.9	4.2	16.1	5.9
Isopropyl alcohol, 91 per cent	13.5	4.0	17.5	2.5	18.2	6.0	24.2	5.1	15.9	4.8	20.7	2.2	11.3	6.2	17.4	7.0
Ether, U. S. P.	10.8	1.0	11.8	7.0	10.0	2.0	12.0	13.8	8.2	0.8	9.0	11.7	17.5	4.0	21.5	14.5
Acetone, U. S. P.	12.3	3.0	15.3	3.2	12.6	3.0	15.6	7.4	11.2	3.3	14.5	4.2	9.8	5.0	14.8	13.1
Carbon tetrachloride, 99.5 per cent	7.6	1.0	8.6	8.3	6.6	0.7	7.4	13.8	4.9	0.8	5.8	12.4	13.0	3.6	16.6	12.1
Ethyl alcohol, 65 per cent	. .	.	18.7				32.6		.		24.4				19.8	
Alkaline 65 per cent ethyl alcohol	....		20.0				30.6				30.7				24.1	

[a] Made with 95 per cent ethyl alcohol after the beans had been practically exhausted with the solvents enumerated in first column.

[b] Made with 80 per cent ethyl alcohol heated just below boiling for 1 hour.

Table II Solubility and Color of Extractive Matter, in Per cent

Solvents	Extractive Matter Soluble in 65 Per cent Ethyl Alcohol[a]								Color of Alcoholic Extracts							
	Based on Weight of Beans				Based on Weight of Total Extractive Matter				Mexican		Bourbon		Tahiti		Tonka	
	Mexican	Bourbon	Tahiti	Tonka	Mexican	Bourbon	Tahiti	Tonka	Red	Yellow	Red	Yellow	Red	Yellow	Red	Yellow
Ethyl alcohol, 95 per cent	12	23	13	13	63	77	61	80	8	38	12	50	5	32	0	2
Isopropyl alcohol, 91 per cent	10	18	16	11	57	74	80	62	5	35	8	40	8	32	1	2
Ether, U. S. P.	1	3	3	0.4	10	27	31	2	0	9	0	10	1	8	0	0
Acetone, U. S. P.	6	7	8	3	38	45	54	22	8	70	8	85	12	62	0	1
Carbon tetrachloride, 99.5 per cent	0.8	0.6	0.5	0.3	9	8	9	2	1	2	0	2	0	0	0	0
Ethyl alcohol, 65 per cent	19	33	24	20	100	100	100	100	28	100	32	157	25	77	3	10
Alkaline 65 per cent ethyl alcohol	20	31	31	24	100	100	100	100	50	112	68	187	62	112	4	10

[a] Does not include vanillin.

erated, were subjected to a further extraction with 200 cc. of 80 per cent alcohol by heating just below boiling for 1 hour, the flasks being closed with funnels. The solvent was then removed at the temperature and pressure noted above and the extractive matter weighed.

The extractive matter from the first two extractions was dissolved in 65 per cent alcohol and united. The resulting twenty solutions were then made up to a volume of 1 liter each with 65 per cent ethyl alcohol, mixed, and filtered through a plug of cotton which removed a considerable amount of black, oily material. The filtrates were reserved for extended examination to determine their analytical characters. Those extracts made directly from the beans with 65 per cent alcohol and with alkaline 65 per cent alcohol were also made up to a volume of one liter and reserved for analysis. The total solids on these solutions were determined at a temperature of 65° C. and pressure of 50 mm., and are reported in Table II as "Extractive matter soluble in 65 per cent ethyl alcohol." These figures do not include vanillin, since the vanillin was volatilized when the extracts were evaporated. In the case of the alkaline 65 per cent ethyl alcohol solution, the weight of the added potassium carbonate was subtracted before reporting the per cent of total solids. The colors of the final extracts obtained with the Lovibond tintometer are also given in Table II.

Discussion of Data

The Bourbon beans yield a considerably larger amount, both of total extractive matter and of extractive matter which is soluble in 65 per cent alcohol, than the Mexican and Tahiti beans with the following solvents: 65 and 95 per cent ethyl alcohol, and isopropyl alcohol. The yields are also larger than those from the Mexican beans with the alkaline 65 per cent ethyl alcohol.

The Tahiti beans yield a considerably larger amount of extractive matter which is soluble in 65 per cent alcohol than the Mexican beans with the following solvents: 65 and 95 per cent ethyl alcohol, isopropyl alcohol, and alkaline 65 per cent alcohol. Therefore, the beans may be rated in the following order—namely, Bourbon, Tahiti, and Mexican—from the standpoint of yield of extractive matter soluble in 65 per cent alcohol, with the solvents enumerated above.

Ether and carbon tetrachloride dissolve out much less total material from the Mexican, Bourbon, and Tahiti beans than the alcoholic solvents. The total extractive matter obtained with acetone is in all cases less than that obtained with the alcoholic solvents, but is substantially more than that obtained with ether and carbon tetrachloride. However, so little of the total extractive matter obtained with ether, acetone, and carbon tetrachloride is soluble in 65 per cent ethyl alcohol, that it appears at this time the use of any of these three solvents is impracticable unless the beans after being exhausted with these solvents are subjected to action of other solvents. The largest amount of extractive matter soluble in 65 per cent alcohol was obtained with acetone and was 8 per cent, whereas the lowest amount obtained with the alcoholic solvents was 10 per cent and the highest amount was 33 per cent. However, the complete evaluation of the quality of the extractive matter is not yet accomplished, and it may be that one or another of these three solvents will make a somewhat better showing from the standpoint of quality than they have from the standpoint of quantity. At the present stage of the investigation the alcoholic solvents are shown to be much superior.

It is interesting to observe that carbon tetrachloride extracts from the beans less than 1 per cent of material (exclusive of vanillin) which is soluble in 65 per cent ethyl alcohol and practically no color which is soluble in 65 per cent alcohol, but does extract a substantial amount of a dark red, viscous, oily material which is insoluble in 65 per cent alcohol. This insoluble material is practically tasteless, and possesses a fatty odor which became rancid on standing. Its saponification numbers were as follows: Mexican, 82; Bourbon, 111; Tahiti, 94. In the authors' opinion this material has little or no value as a flavor, although their attention has been called to a patent[3] the claims of which indicate that certain insoluble material obtained under somewhat the same conditions has a substantial flavoring value. It is reported[4] that in the preparation of a pure extract the use of alcohol weaker than 45 per cent is not commercially practicable owing to difficulties in percolation. A process which involves a preliminary extraction with carbon tetrachloride, followed by extraction with a weak alcoholic solution, is promising, since it is believed that the removal of the black, oily material will facilitate subsequent percolation. This process is now being subjected to a special investigation.

About the same quantities of total extractive matter are obtained from tonka beans by each of the solvents. However, the alcoholic solvents yield more extractive matter that is soluble in 65 per cent alcohol than does ether, acetone, or carbon tetrachloride. Here, too, there is a possibility of obtaining an advantage by making a preliminary extraction of the beans with ether or carbon tetrachloride, and a subsequent extraction with a weak alcoholic solution.

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[3] U. S. Patent 931,805 (August 24, 1909).

[4] Leach, "Food Inspection and Analysis," 4th ed., p. 914.

The analytical characters of the final extracts are now being determined and it is proposed also to determine the relative flavoring quality of the extracts made with the different solvents by comparing the taste of custards, junket, cakes, beverages, and other edible material to which the extracts have been added.

Adsorption of Color from Sugar Solutions by Chars[1]

By **Marshall T. Sanders**

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At the fall meeting of this Society in 1921, F. W. Zerban presented a paper in which he showed conclusively that the action of decolorizing carbons in removing color from sugar and molasses solutions can be expressed by Freundlich's adsorption equation $X/M = KC^{1}/^{n}$, where X = the amount of solute adsorbed by M grams of carbon, C is the concentration of the solute at equilibrium, and K and n are constants. He further showed that the "color units" proposed by Meade and Harris[2] could be used in place of the concentration terms X and C. Unfortunately, Dr. Zerban has not as yet published this paper.

At this laboratory it has also been found that the color removal by vegetable carbons follows the Freundlich equation in the cases of sugar and molasses solutions.

Plate I shows the relation between the percentage of color removed from a certain molasses solution and the weight of the carbon used. Since 2 grams of carbon do not remove twice as much color as 1 gram, it is obvious that the carbon did not do as much work per gram when the larger quantity was used as it did with the smaller quantity.

The term X/M in the Freundlich equation is really the work done by a unit weight of carbon. This equation states that the work done by a unit weight of carbon (X/M) is proportional to some power of the concentration of the solute at equilibrium.

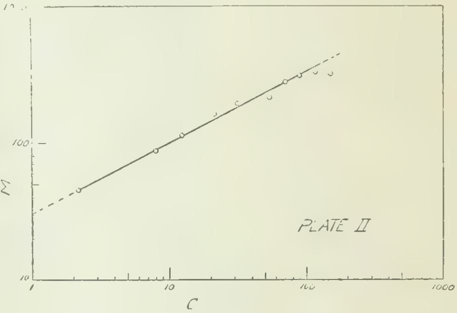
Taking the logarithms of both sides of the equation, we have

$$\text{Log } X/M = 1/n \log C + \log K$$

If log X/M and log C are considered as variables, the equation is of the type $Y = AX + B$, or that of a straight line.

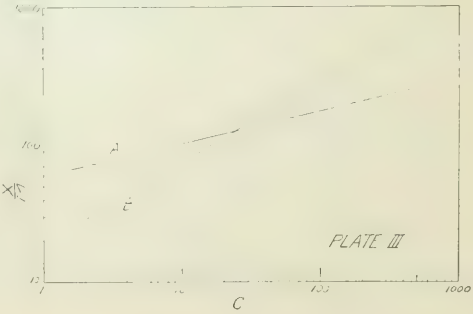
A plot of X/M vs. C on double logarithmic cross-section paper is given in Plate II for the same data as were used in preparing Plate I, with the exception that in Plate II color units are used instead of percentage of color. Curve C, Plate IV, is for the data in Plate I, with the color expressed as per cent.

Any errors in determining the color of the solutions at the left-hand end of the curve cause approximately a horizontal displacement of the points, at the right-hand end a nearly vertical displacement.



An inspection of Plate II will make clear the fact that, whenever it is possible to use them, countercurrrent methods of decolorization would reduce the amount of carbon consumed by a given quantity of a solution. The right-hand side of the plot corresponds to dark solutious.

The value of the expression X/M is much greater for the slightly than for the greatly decolorized solutions. X/M is the amount of coloring matter, or color, if we may use that term, which is adsorbed by a given weight of carbon. If the fresh carbon is brought into contact with a partially decolorized solution and leaves the system practically in equilibrium



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[1] Presented before the Division of Sugar Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923, by Mr. Sanders instead of Mr. Bonnet as indicated on the program.

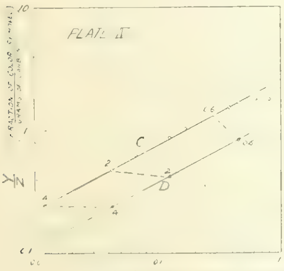
[2] This Journal, **12**, 687 (1920).

with the undecolorized solution, it is obvious that it has removed more color per unit weight than if the treatment were given in one stage and the carbon were separated from a highly decolorized solution.

Suppose the action of two carbons on a solution is as represented in Plate III. For high degrees of decolorization in a single application, *A* would be superior to *B*, weight for weight, at the point of intersection they would be equally efficient, and for low degrees of decolorization or counterflow work *B* would be superior to *A*. All other things being equal, *A* would be chosen if a high degree of decolorization were desired in one application of the carbon, *B* would be superior for countercurrent decolorization.

The values for two carbons of the function X/M at any final concentration, C, represent the relative work done by the carbons to obtain that degree of decolorization. It follows that if one carbon adsorbs more color per gram than another, less of it than of the poorer carbon will be required in any given case.

A consideration of these logarithmic plots shows the fallacies of certain methods of testing carbons. These methods are used by some companies or are given in the various journals, and have come to the attention of this laboratory from time to time. One of these is to weigh out 1 gram of carbon, suspend it in 100 cc. of water, and add a dye solution until the color is just perceptible in the supernatant liquor after the carbon has settled, or until the color appears when a drop is "spotted" on filter paper. This is equivalent to measuring the value of X/M for some final color, C, which is barely perceptible. This method is faulty for two reasons—first, the method determines only one point on the curve; second, the final color is not fixed. The color should be determined by matching with some standard.



The use of the term "decolorizing power" is misleading. This value is generally determined for only one weight of carbon under certain set conditions. This is equivalent to determining one point on the curve, but tells nothing of its direction.

To say that a carbon is twenty times as efficient as another is equally valueless, since the relative efficiencies of two carbons may vary with different solutions and even with different initial concentrations of the same solute and solvent.

Some tests which have come to our attention are not only faulty in that they try to compare two carbons by a simple ratio, but also because too great samples of carbon are used and the decolorization is practically complete for both.

In Plate IV are shown the lines of constant carbon when plotted on the logarithmic paper, and the per cent decolorization is used instead of the color units. These curves hold only for a series of carbons which give parallel graphs. One could be easily mislead by using too large samples of carbon for a comparison by means of a single determination.

The 4-gram line cuts Curve *C* at 98.8 per cent and Curve *D* at 96 per cent decolorization. This would seem to indicate about equal efficiencies for the carbons, yet carbon *C* is twice as efficient as carbon *D* for any given degree of decolorization.

Another method given in the literature[3] is one in which a series of solutions of different degrees of decolorization is made by the use of various weights of a standard carbon. A certain weight of the unknown carbon is used to treat the standard molasses solution and the decolorized solution is matched with the samples prepared by use of the standard carbon. The relative weights of the standard and unknown carbons used to obtain the same degree of decolorization are taken as a measure of the efficiency of the unknown carbon. This method assumes that the adsorption curves of the two carbons are parallel, which may not be the case, and has the objection that only one point on the curve is determined.

The use of the Freundlich equation will enable one to determine the relative decolorizing capacity of the various carbons with the minimum number of tests. It would seem needless to state that the samples of carbon should be taken on a dry basis; yet two or three cases have come to our attention where the carbons were weighed out as received. Carbons can readily absorb up to 10 or 15 per cent moisture. It is obvious that the results of such tests are misleading.

In the present state of our knowledge concerning the action of decolorizing carbons, there should be no attempt to arbitrarily rate one carbon in terms of another. The user should test out the carbons on the solution he intends to decolorize.

In choosing a carbon, other factors than its decolorizing ability must be taken into consideration. The apparent density of the carbon, its filterability, and its staying or lasting qualities must also be considered. The user is interested, not in any one of these properties alone, but in decolorizing his solution at the minimum cost and, consequently, greatest profit.

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[3] This Journal, **14**, 19 (1922).

Calculations for Decolorizing Carbons[1]

[Supplementary to Preceding Article.]

By **M. T. Sanders**

Atlas Powder Co., Wilmington, Del.

In working with decolorizing carbons, it is very desirable to be able to calculate the mass of carbon necessary for a given degree of decolorization. It has been shown[2,3,4] in the case of sugar solutions, that Freundlich's adsorption equation is applicable to color removal by vegetable chars. This equation as used is:

$$X/M = KC^{1/n}$$

where X = Units of / Fraction of } color removed by M grams of carbon

C = Units of / Fraction of } color remaining in decolorized solution

K and $1/n$ are constants depending on the amount and kind of solution treated with the carbon.

To determine the constants K and $1/n$, several equal volumes or masses of the solution in question are treated with various quantities of carbon. These quantities of carbon are so chosen as to give a series of values of log C with approximately equal increments, these values being taken over a range corresponding to from 20 to 95 per cent decolorization. The values of X/M and C are computed and these values plotted on the so-called double logarithmic paper. The author prefers to use the fraction of decolorization instead of units of color, because by so doing a piece of logarithmic paper 10 inches square, with two 5-inch scales on each axis, is sufficient to take care of all data from 0 to 99 per cent decolorization.

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[1] Received June 19, 1923.

[2] Zerban and Byall, "Adsorption Isotherms of Some Decolorizing Carbons." Presented before the Section of Sugar Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 9, 1921.

[3] Sanders, *Chem. Met. Eng.*, **28**, 541 (1923).

[4] Sanders, "Adsorption of Color from Sugar Solutions by Chars," preceding article.

The use of logarithmic paper made on a 10-inch base has the further advantage that $1/n$ can be scaled directly from the plot. K of course is read where $C = 1.0$. The determination of the constants graphically is illustrated in Fig. 1.

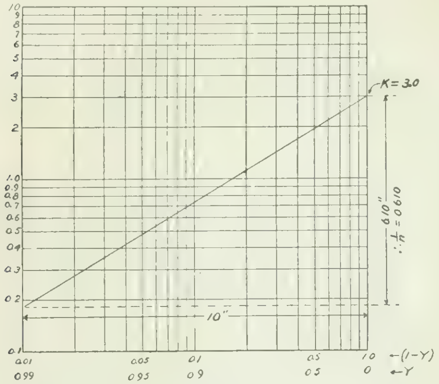

FIG. 1

In calculating the degree of decolorization, the author prefers to use a system described by him in a previous paper.[3] It will be noticed that there is no way of reading directly from the chart the mass of carbon required for any given degree of decolorization. True, one can read the values of X/M and C, and from the relation $X + C = 1$ (if color is expressed as a fraction of the original color) calculate the corresponding value of M.

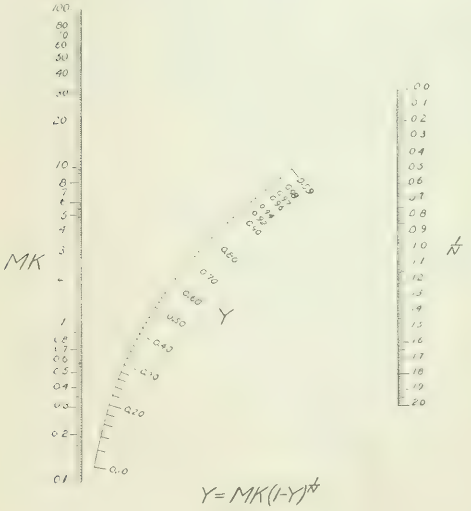

FIG. 2

However, this may be done more easily. The nomographic chart, Fig. 2, solves the equation $Y/M = K(1-Y)^{1/n}$. This equation is the same as $X/M = KC^{1/n}$, if we express our color as a fraction of the initial color, and let $X = Y$, for then $C = 1-Y$.

To use this chart, suppose that experiment shows that for the solution in question the values of K and $1/n$ are 3 and 0.610, respectively. We wish to know how much carbon is necessary to remove 70 per cent of the color. On Fig. 2 draw a straight line from $1/n = 0.610$ to $Y = 0.70$, and extend this line to the MK axis. The line (extended) cuts the MK axis at 1.45. Since $K = 3$, then $M = 1.45/3 = 0.483$ grams or pounds of carbon per unit volume of solution, depending on what units of mass and volume were used in securing the adsorption data. Before a carbon can be described in terms of K and $1/n$ for any solution, it will be necessary to adopt standards of mass and volume for the carbon and solution, respectively.

The author would suggest the adoption of the following system for calculating the values of K and $1/n$. Use the equation

$$Y/M = K(1-Y)^{1/n}$$

where M = fraction of carbon by weight added to the solution to be decolorized

Y = fraction of color removed by the carbon of weight M

K and $1/n$ are the constants to be listed in describing the carbon.

This system has the advantage that the values of K and $1/n$ as found in the laboratory are applicable to plant calculations without the use of any conversion factor.

This last should be a matter for some section of the AMERICAN CHEMICAL SOCIETY to take up, presumably the Sugar Division, as it seems the most interested in decolorizing carbons.

Variation of Refractive Index of China Wood Oil with Temperature[1]

By F. H. Rhodes and H. E. Goldsmith

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THE refractive indices of two samples of China wood oil have been determined at various temperatures. Sample 1 was from a lot of commercially pure China wood oil (from S. C. Gilespie & Sons). Sample 2 was from a portion of China wood oil of known purity brought directly from China by S. H. Shen, and donated to us for use in this work.

The refractive indices were determined by means of a refractometer provided with a water jacket through which water at a constant temperature was circulated. The instrument was tested with liquids of known refractive indices, and was found to give correct readings.

The results obtained were as follows:

Temp C	Sample 1 Refractive Index	Sample 1 Difference	Sample 2 Refractive Index	Sample 2 Difference
10	1.5196		1.5235	
		> 0.0040		> 0.0040
20	1.5156		1.5195	
		> 0.0039		> 0.0040
30	1.5117		1.5155	
		> 0.0039		> 0.0039
40	1.5078		1.5116	

From these results it is apparent that the refractive index of China wood oil decreases 0.000395 for each increase of 1° C. in the temperature. This result agrees very closely with the value of 0.0004 obtained by Browne[2] from the examination of a single sample of oil through a single temperature interval.

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[1] Received May 18, 1923.

[2] *Chem. News*, **114**, 123 (1916).

Determination of Sugar in Cossettes by the Pellet Method[1]

Volume Allowance for Marc and for the Combined Marc and Lead Precipitate

By S. J. Osborn

Sugar Building, Denver, Colo.

Determinations of the amount and specific gravity of the marc, and of the combined marc and lead precipitate, were made on Colorado and Nebraska beets of the 1922–23 campaign. The volume allowance for the marc in 26 grams of beets was found to be 0.6 ml., and for the combined marc and lead precipitate 0.9 ml. The beets of the campaign in question contained less than the normal percentage of marc.

IN THE determination of sugar in cossettes by the Pellet method of hot water digestion, the normal weight, 26 grams, is made up to a volume of 200 ml. of liquid. The flask is graduated to allow for the marc, or insoluble matter, which occupies a portion of the volume. While the volume allowance for the marc is variously stated,[2] the method generally employed considers the volume of the marc in 26 grams of beets to be 0.6 ml., and the flask is accordingly graduated at 200.6 ml. This is the volume allowance prescribed in most of the standard methods of analysis. Pellet,[3] however, in 1906 recalculated the data, with the conclusion that 0.8 was a more accurate figure.

It has long been recognized that marc is capable of no strict definition, since some of the marc constituents are partially soluble in water, and the amount of marc found depends on the amount of washing and other conditions of the method employed. Fortunately, variations due to such causes or variations actually existing in the beets have a relatively small influence on the accuracy of the sugar determination, so that it is possible to establish and use an average value for the volume allowance without serious error.

It is not clear why the volume allowance has always been based on marc alone and the volume of the lead precipitate has been generally neglected. As there seemed to be no good reason why the volume allowance should not take account of both the marc and the lead precipitate, determinations were made, on the one hand, of marc alone, and on the other, of the combined marc and lead precipitate. The work was carried out on beets grown in northern Colorado and western Nebraska of the 1922–23 campaign.

Claessen's method[4] was used for the marc determination, with the employment of a piece of linen cloth as a filtering medium. Briefly described, this consists of extracting 26 grams of ground beets four times with 400 ml. of boiling water, allowing a period of digestion of 2 minutes in each case. The residue was washed with a little alcohol and dried at 105° to 110° C. The combined marc and lead precipitate was determined by transferring the entire insoluble residue from a hot water digestion to a filter paper, washing until free from sugar with cold water (about 1 liter), and drying at 105° C. In this operation some solution of the lead precipitate could not be entirely avoided.

In the specific gravity determinations, water, ethyl alcohol, and methanol proved unsuitable on account of their solvent action on the marc and the lead precipitate. This action was more pronounced on the dried material. Xylene was found to be a suitable liquid for the pycnometer weighings, and was employed, except as otherwise noted. It has no solvent action and was preferred to benzene on account of its higher boiling point. A very important part of the technic lies in the removal of occluded air from the marc. This seemed to be satisfactorily accomplished by placing the pycnometer under a good vacuum for 30 minutes.

The average results are given in tabular form. In the fourth series the specific gravity was determined by weighing the wet marc in water and drying afterwards to establish the weight taken. This avoids the difficulty of removing occluded air, but is open probably to some error caused by the solvent action of the water.

It will be noted that the percentages of marc found in this work are unusually low. This was undoubtedly a characteristic of the beets of the campaign in question, which were considerably below the average in sugar content. Wohryzek[5] has used Skärblom's data to show that beets low in sugar are also low in marc, and vice versa. A general relation of this kind has also been established from the writer's own experience. On western Nebraska beets of another campaign—viz., 1920–21—the average of 114 determinations gave 4.39 per cent marc by Claessen's method.

The following comparative determinations of the specific gravity of dried marc were made in water and in xylene.

Series No.	No. of Tests	Sp. Gr. in Water	Sp. Gr. in Xylene
1	3	1.582	1.488
2	5	1.597	1.534

CONCLUSIONS

The probable experimental errors, due to solubility of the marc and lead precipitate and possible loss of particles in filtration, would tend to make the volume found too low. However, it is likely that these errors are no greater than the actual variations which will be found in different beets at

AVERAGES OF MARC INVESTIGATIONS

Series No.	District	No. of Tests	Sugar	Purity	Marc %	Marc Sp. Gr. 20°/4°	Marc Volume[a] Ml.	Marc Plus Lead Precipitate %	Marc Plus Lead Precipitate Sp. Gr. 20°/4°	Marc Plus Lead Precipitate Volume[a] Ml.	Liquid Used in Sp. Gr. Detn.
1	Colorado	74	14.80	83.47	3.33	1.470	0.589	6.97	2.074	0.874	Xylene
2	Colorado	42	13.89	81.39	3.60	1.519	0.616	7.34	2.079	0.917	Xylene
3	Nebraska	16	14.8	85.4	3.83	1.433	0.694	7.06	2.073	0.886	Xylene
4*A*[b]	Nebraska	24	14.41	84.3	3.55	1.588	0.582	7.82	2.513	0.814	Water
4*B*[b]	Nebraska	24	14.41	84.3	3.55	1.593	0.580	7.82	2.383	0.854	Water

[a] In 26 grams of cossettes.

[b] In Series *A* the specific gravity was determined by weighing the wet, extracted material in a pycnometer, and drying afterwards. In Series *B* the specific gravity was redetermined on the dried residues.

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[1] Presented before the Division of Sugar Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Browne, "Handbook of Sugar Analysis," p. 246.

[3] *Z. Ver. deut. Zucker-Ind.*, **56**, II, 912 (1906).

[4] *Ibid.*, **66**, II, 359 (1916).

[5] "Chemie der Zuckerindustrie," p. 36.

various times. The results are all in close enough agreement to warrant the following conclusions:

1—On the basis of the 1922–23 results, the volume of marc in 26 grams of cossettes is very close to 0.6 ml., so that, if the cossette flask is graduated to take account of marc alone, its capacity should be 200.6 ml., the volume now usually employed. If the flask is graduated to take account of the combined marc and lead precipitate, and there seems to be no good reason why this is not a better basis than the marc alone, the volume should be 200.9 ml.

2—The 1922–23 beets are abnormally low in marc as well as sugar. A range of 4.00 to 4.25 per cent would probably not underestimate the average marc content of Colorado and Nebraska beets. With a marc content of 4.00 to 4.25 per cent, the volume allowance for the combined marc and lead precipitate would be about 1.0 ml., and the cossette flask should accordingly be graduated at 201.0 ml.

3—The employment of a volume of 201.0 ml. for the cossette flask in place of 200.6 ml. would lower the polarization of a 16 per cent beet to the extent of 0.03. The error under the present volume allowance is therefore almost negligible, but there is no reason why the cossette flask should not be regraduated to conform with the best available data.

ACKNOWLEDGMENT

The writer's thanks are hereby expressed to C. C. Crawford, Geo. Goldfain, G. E. Stevens, and J. H. Zisch for the experimental data and ideas developed in the course of the investigation.

Conversion of Methyl Chloride to Methanol—II[1]

By Ralph H. McKee and Stephen P. Burke

COLUMBIA UNIVERSITY, NEW YORK, N. Y.

In Part I the authors have shown, both experimentally and theoretically, that it is impossible to effect the direct hydrolysis of methyl chloride to yield methanol by means of steam alone. An experimental investigation of the use of metallic hydroxides to effect this conversion was described, and it was shown that calcium hydroxide is the most advantageous. By passing methyl chloride mixed with steam over calcium hydroxide at elevated temperatures, 95 per cent of the methyl chloride is converted into methanol and methyl ether, the remainder undergoing decomposition. A theoretical study of the reacting system was made and by means of an approximate calculation of the free energy relationships (Nernst's heat theorem) the equilibrium points of the reactions involved were determined. The experimental results have been found to be in very good agreement with the theoretical values.

In this article the simultaneous or side reactions encountered are studied, and detailed analyses of the factors and conditions influencing the conversion of methyl chloride to methanol are made. A catalytic process for the conversion to methanol of the methyl ether obtained as a by-product is presented. In conclusion, a brief rationale of the process is given and estimated production costs of methanol by this process are shown.

IN ORDER to interpret the results obtained in the experimental work described in Part I, it was found necessary to investigate in some degree the simultaneous reactions occurring in the reaction chamber.

$$Ca(OH)_2 = CaO + H_2O \quad (1)$$

In order to determine whether, under the conditions obtaining during the runs discussed in Part I, any decomposition of the calcium hydroxide took place, the calcium hydroxide and chloride residues were examined for the presence of calcium oxide in many cases where anhydrous methyl chloride was used in the experiment. Its presence was detected only in very small amounts at 400° and 450° C. This was to be expected, however, for at 350° C. the partial pressure of water due to this decomposition does not exceed 14 mm.[2] It may be pointed out here that under these conditions magnesium hydroxide would be very unstable, for the partial pressure of water from magnesium hydroxide becomes equal to one atmosphere at a temperature slightly above 200° C. For this reason it is far less desirable than calcium hydroxide in effecting the conversion of methyl chloride.

$$CaCl_2 + H_2O = Ca(OH)_2 + 2HCl \quad (2)$$

No quantitative data on the extent of this reaction could be found in the literature. Therefore, a number of experiments were performed at 350° C., with partial pressures of water in excess of 600 mm. These experiments were carried out using part of the apparatus shown in Fig. 1 of Part I. The reaction tube was charged with C. P. anhydrous calcium chloride (containing approximately 10 per cent moisture) of 12-mesh size. Air was passed slowly through the humidifier heated to 93° C. (vapor pressure of water = 590 mm.), and thence through the reaction chamber, and on through the absorption bulbs containing distilled water with a few drops of phenolphthalein. The hydrogen chloride produced by the reaction was collected in the absorption train, and at equal time intervals it was titrated with standard 0.1 *N* sodium hydroxide. The results obtained show that under these conditions, even at vapor pressures exceeding 600 mm., over a period of time greatly in excess of that required for the conversion of methyl chloride, the hydrolysis of calcium chloride would not exceed 2.5 per cent by weight. Thus, it can be concluded that the hydrolysis of the calcium chloride formed in the reaction

$$Ca(OH)_2 + 2CH_3Cl = CaCl_2 + 2CH_3OH \quad (3)$$

by the presence of steam is practically inappreciable, and hence, that the displacement of the equilibrium of this reaction is negligible. Any displacement of the equilibrium to the right due to the hydrolysis of calcium chloride would probably be neutralized by the immediate reaction of hydrochloric acid with methanol.

STUDY OF REACTION: $CaCl_2 + 2CH_3OH = Ca(OH)_2 + 2CH_3Cl$—This reaction, which is the reverse of that used to effect the conversion of methyl chloride to methanol, was investigated to determine the extent to which it could be carried out. The experimental method used here was very similar to that employed in the investigation of the hydrolysis of calcium chloride. The reaction tube was filled with C. P. anhydrous calcium chloride, and air was sent slowly through the humidifier and on through the reaction tube. In this case, however, the humidifier contained absolute methanol. The partial pressure of the methanol was maintained as near to one atmosphere as possible. The absorption train was replaced by a 4-liter gas collection bottle, and the gases produced were collected directly. Several experiments were run with the same result. The methanol used (50 grams) was

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[1] Received December 4, 1922. Part I, THIS JOURNAL, **15**, 682 (1923).

[2] Dragert, Inaugural Dissertation, University of Berlin, **1914**.

almost quantitatively recovered. A very small amount of gas (less than 100 cc.) was obtained, which proved to be partly methyl ether. Methyl chloride, if produced, was too small in amount to be positively identified.

Since there was a possibility that Ca(OH)Cl, or some similar compound other than $CaCl_2$, was the principal end product obtained during the conversion of methyl chloride to methanol, these experiments were repeated, using the residue remaining in the reaction chamber after one of the conversion runs. The results in this case were practically the same as those obtained when using calcium chloride. It is evident, of course, that these results are quite in accord with the calculations based on Nernst's theorem, given in Part I. According to the calculated equilibrium point, even if equilibrium were attained here, the methyl chloride formed would be less than 2 per cent of the methanol used (= 400 cc. methyl chloride). The formation of the small amount of ether was probably due to a secondary reaction (Reaction 10).

Pyrogenetic Decomposition of Methanol—The decomposition of methanol under the action of heat has been investigated, and it has been shown that this alcohol is the most stable of the primary alcohols toward heat.[3] On passing the vapor of methanol through glass tubes, decomposition begins only above 700° C., according to the reaction:

$$CH_3OH \longrightarrow CO + CH_4 + H_2 \qquad (4)$$

This result has been confirmed by other investigators.[4] However, in the presence of catalytic agents it has been shown that methanol decomposes at 300° C., according to the equations[5]

$$2CH_3OH = CH_3.O.CH_3 + H_2O \qquad (5)$$
$$CH_3OH = HCHO + H_2 = CO + 2H_2 \qquad (6)$$

Which of these reactions predominates depends upon the nature of the catalyst present.

Apparently, no appreciable simultaneous decomposition of the methanol formed takes place under the conditions of our experiments except above 400° C. The low temperature employed and the absence of carbon monoxide exclude Reaction 4. The small amounts of methane and hydrogen obtained are probably principally the result of the decomposition of methyl ether and methyl chloride, as shown below. Likewise, the absence of formaldehyde (except in traces) proves the absence of Reaction 6. While a considerable quantity of methyl ether was formed, it cannot be attributed to Reaction 5, for when methanol vapor was passed over calcium hydroxide and chloride in the experimental work described above, methyl ether was formed in very small amounts, although the conditions here were much more favorable for its formation according to Reaction 5. Moreover, from the results of Sabatier's work we would not expect any of the substances present in the reaction chamber to catalyze this reaction. The formation of the methyl ether obtained is caused by a different reaction to be explained later.

Pyrogenetic Decomposition of Methyl Chloride—Different observers working under various conditions have obtained various combinations of decomposition products of methyl chloride. At high temperatures one observer[6] reports

$$CH_3Cl \longrightarrow C + C_{10}H_8 + C_2H_4 + CH_4 + (HCl?)$$

On passing methyl chloride over reduced nickel at 220° C., carbon, hydrogen, and hydrogen chloride are obtained.[7] However, no previous work was found on this decomposition under the conditions obtaining in our reaction chamber, and so a brief experimental investigation was carried out.

The commercial methyl chloride was passed through the apparatus shown in Fig. 1, Part I, the reaction tube being filled with pure silica sand. Trials were made at temperatures of 200°, 300°, 400°, and 500° C., using rates about the same as those employed in the conversion runs. It was found that while decomposition was observable by the formation of traces of carbon and hydrogen chloride at 300° C., it did not become appreciable until 400° C. The results obtained are shown graphically by Curve 12*A*. The analysis of the gas received showed that methane was formed, but that hydrogen and ethylene were absent. Carbon and hydrogen chloride were also formed. Hence, under these conditions the reaction probably is

$$2CH_3Cl \longrightarrow C + 2HCl + CH_4 \qquad (7)$$

It has been observed that barium chloride acts catalytically in the decomposition of ethyl chloride under similar conditions.[8] Hence, the foregoing experiments were repeated, using calcium chloride instead of silica in the reaction tube, to determine whether the former had any catalytic effect. The decomposition was not increased, however.

Study of Reaction: $CH_3OH + HCl = CH_3Cl + H_2O$ (8)—This reaction, which is the reverse of the direct hydrolysis of methyl chloride by steam, has already been fully discussed, and it has been shown that the equilibrium point is far over to the right. Hence, this reaction will occur in the reaction chamber when high partial pressures of steam are used, because the resulting slight hydrolysis of calcium chloride will give rise to the formation of some hydrogen chloride. But since the amount of hydrogen chloride so produced is extremely small, the re-conversion to methyl chloride effected by this reaction must be very slight.

Study of Reaction: $CH_3OH + CH_3Cl = (CH_3)_2O + HCl$ (9)—Since the formation of methyl ether was not due to the dehydration of methanol (Reaction 5), this reaction suggested itself as its source. However, considering the equilibrium from a theoretical point of view in the light of Nernst's theorem, it was shown above that

$$K = \frac{CH_3OH \times CH_3Cl}{(CH_3)_2O \times HCl} = 0.0006$$

That is, equilibrium is far over to the left, and hence, if our assumptions are correct, this reaction could not possibly give rise to the amounts of methyl ether obtained.

In order to verify this conclusion, an experimental determination of the extent of this reaction was made under the conditions prevailing during the conversion runs. The apparatus shown in Fig. 1, Part I, was used. The methyl chloride, after leaving the meter, passed through the drying train and then through the humidifier and on through the entire apparatus. The reaction tube was filled with glass beads. The humidifier contained absolute methanol, and methyl chloride was passed through the reaction chamber, which was filled with glass beads (temperature, 350° C.). A small amount of distilled water was placed in one of the absorption bulbs to absorb the hydrogen chloride formed. The temperature of the humidifier was maintained at 48° C., so that an equimolecular mixture of methyl chloride and methanol was sent through the reaction tube.

The results obtained were in excellent accord with the theoretical conclusion. The methyl chloride was almost quantitatively recovered (a small amount dissolved in the water of the absorption train). The amount of hydrogen chloride obtained was determined by analyzing the water of the absorption bulbs for chloride, and from the amount of hydrogen chloride so determined the extent of the reaction was computed on the assumption that equilibrium conditions had been obtained. The result obtained was K_p(350° C.) = 0.000008. This result is seen to be much smaller than the equilibrium constant derived above on the basis of Nernst's theorem [K_p(350° C.) = 0.0006]. A discrepancy in this direction is to be expected, however, for undoubtedly equilibrium was not attained here. The experimental result obtained corresponds to an approach of 12 per cent to the equilibrium point calculated by Nernst's formula.

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[3] Ipatjew, *Ber.*, **35**, 1056 (1902).

[4] Bone and Davis, *J. Chem. Soc.* (*London*), **105**, 1691 (1914).

[5] Sabatier and Maihle, *Ann. chim. phys.*, **20**, 289 (1910).

[6] Perrot, *Ann.*, **101**, 375 (1857).

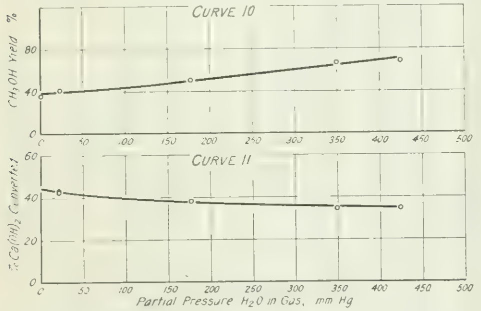
[7] *Compt. rend.*, **138**, 407 (1904).

[8] Sabatier and Maihle, *Compt. rend.*, **141**, 238 (1905).

Further evidence for this conclusion is given by the observation of Kuenen[9] that an irreversible reaction takes place slowly between methyl ether and hydrogen chloride at 100° C., with the formation of water and methyl chloride, and that the velocity of this reaction increases very rapidly with the temperature. This reaction is very probably the result of the two reactions

$$CH_3.O.CH_3 + HCl = CH_3OH + CH_3Cl \qquad (9)$$
$$CH_3OH + HCl = CH_3Cl + H_2O \qquad (8)$$

both of which, according to the experimental and theoretical observations already made, have their equilibrium points far to the right—that is, according to our calculations, methyl ether and hydrogen chloride *should* combine to give methyl chloride and water with methanol as an intermediate product. The presence of methanol as an intermediate product was probably overlooked.



However, while Reaction 9 alone will not account for the formation of methyl ether, since a hydroxide is present in the reaction chamber during the conversion of methyl chloride, it is to be expected, by analogy to the reactions,

$$CH_3Cl + H_2O = CH_3OH + HCl \qquad (9)$$
$$2CH_3Cl + Ca(OH)_2 = 2CH_3OH + CaCl_2 \qquad (3)$$

that the reactions

$$2CH_3Cl + 2CH_3OH = CH_3.O.CH_3 + 2HCl \qquad (9)$$
$$2HCl + Ca(OH)_2 = CaCl_2 + 2H_2O \qquad (2)$$

which may be regarded as

$$2CH_3Cl + 2CH_3OH + Ca(OH)_2 = 2CH_3.O.CH_3 + 2H_2O + CaCl_2 \qquad (10)$$

would result in the formation of considerable amounts of methyl ether. This conclusion is strongly confirmed by the application of Nernst's theorem, which gives as the equilibrium point

$$K_p(350° \text{ C.}) = \frac{(CH_3.O.CH_3) \times H_2O}{CH_3Cl \times CH_3OH} = 250 \text{ (see Part I)}$$

This reaction, then, is the probable source of the methyl ether obtained.

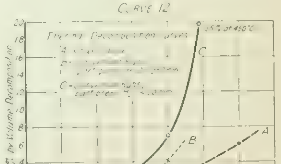
CONDITIONS INFLUENCING THE CONVERSION

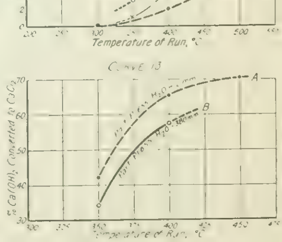
In the light of the foregoing investigation of the nature and extent of the various simultaneous reactions taking place in the reaction chamber, it is possible to study and interpret the effect of certain variables on the conversion of the methyl chloride.

Size of Calcium Hydroxide Granules—In order to determine whether the size of the calcium hydroxide granules had any influence on the extent of the conversion of methyl chloride, duplicate runs were carried out using granules of 4 to 10 mesh in one case and 20 to 50 mesh in the other. The results obtained show that over this range the size of the granules used had no effect. The same conclusion was obtained by carrying out runs using a mixture of approximately 8 and 50-mesh granules. On the completion of the runs the solid residue was screened, and the chloride content of the largest and smallest granules determined separately. In every case the results showed that the chloride content of the granules was the same.

It must be concluded from this that the conversion of calcium hydroxide to calcium chloride is not a surface phenomenon, but that it proceeds fairly uniformly throughout the granules. This conclusion was substantiated by a microscopic examination of the granules removed from the reaction chamber at the completion of a run. As already explained, these particles were gray due to the deposition of carbon resulting from the thermal decomposition of the methyl chloride. Under the microscope it was seen that this gray color extended uniformly over the entire cross section of the granules, thus showing that the methyl chloride had diffused uniformly throughout the entire volume.

On examining Curve 13, which shows the relation between the extent of the conversion of calcium hydroxide to calcium chloride and the temperature, it is seen that as the temperature increases this conversion increases. This increase is to be expected if the mechanism of the conversion depends upon the diffusion of the methyl chloride through the hydroxide granules, for as the temperature increases the coefficient of diffusion increases very rapidly. It appears from this evidence, then, that at any one temperature the methyl chloride diffuses rapidly and quite uniformly through the larger pores of the granules. Diffusion into the smaller pores takes place more slowly, and therefore, when this initial rapid diffusion is complete, the percentage conversion of the methyl chloride falls off rapidly to a small, fairly constant amount, representing the slow diffusion of the gas into the smaller pores of the calcium hydroxide. At a higher temperature diffusion is more rapid, and the gas is able to penetrate the granules more completely before the rate of conversion of the methyl chloride falls to its final small value. In other words, as the temperature increases the effective volume of the calcium hydroxide exposed to the gas is increased.





Velocity of Gas Flow—While very little experimental work was devoted to this factor, yet some indication of its effect can be obtained when Curve 1 (rate = 55 cc. per min.) is compared with Curve 6 (rate = 90 cc. per min.). The general shape of the reaction curves is practically the same. The percentage conversion of the methyl chloride was not reduced by the almost doubled velocity, nor was the relative yield of products affected, except that the thermal decomposition of the gas was decreased. It is evident, therefore, that the space-time yields can be considerably increased over those obtained in this work. Moreover, there is the added advantage that the thermal decomposition of the unconverted methyl chloride is decreased owing to the shorter time of contact with the hot reaction chamber.

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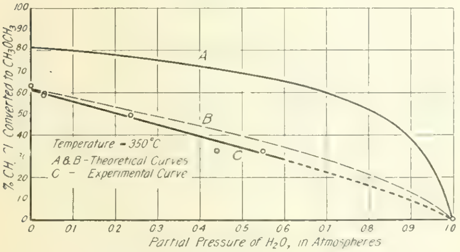
[9] Z. physik. Chem., **37**, 485 (1901).

Effect of Temperature—The temperature is the most significant variable governing the nature and relative amounts of the products obtained. Since the equilibrium points and the relative velocities of the two principal reactions resulting in the formation of the methyl ether and methanol do not change appreciably over the range of temperatures investigated, the general course of the methyl chloride conversion should not change. That this is the case is shown by the curves for Runs 1, 8, and 9, all of which have the same general shape. For the same reason the ratio of the yield of alcohol to that of ether should be the same for similar conditions of humidity, which the data in Table I show to be true. The combined yield of alcohol and ether falls off as the temperature increases, on account of the pyrogenetic decomposition of the methyl chloride and methyl ether.

Curve 14



In the investigation of this thermal decomposition of methyl chloride previously described, it was found that the extent of decomposition increased with the temperature, as shown by Curve 12*A*. From the data obtained in the conversion runs (Table I, Part I), Curves 12*B* and 12*C*[10] were plotted, showing the percentage decomposition of the methyl chloride passing through the reaction chamber, on the assumption that all the methane collected was formed by this decomposition. A comparison of these curves shows that the decomposition occurring at high temperatures is considerably in excess of that given by methyl chloride alone (Curve 14*A*). This must be attributed to a simultaneous decomposition of methyl ether, which, while present at 350° C., only becomes appreciable at 400° C. At 450° C., from the amounts of hydrogen and methane received, it is very significant.

The most important effect of the temperature, however, is the variation it causes in the percentage of calcium hydroxide utilized, as shown by Curve 13. This phenomenon has already been discussed in a previous section (Size of Calcium Hydroxide Granules).

Effect of Partial Pressure of Water Vapor—The most significant result brought about by a variation of the partial pressure of water vapor in the reaction chamber was the effect it produced on the relative yields of ether and alcohol. Curve 14*C* shows graphically the results obtained. As previously explained, the formation of methyl ether must be attributed to the reaction

$$Ca(OH)_2 + 2CH_3Cl + 2CH_3OH = 2(CH_3)_2O + 2H_2O + CaCl_2 \qquad (10)$$

which may be considered as occurring directly, or as the sum of

$$2CH_3Cl + 2CH_3OH = 2(CH_3)_2O + 2HCl \qquad (9)$$
$$2HCl + Ca(OH)_2 = CaCl_2 + 2H_2O \qquad (2)$$

Now, since at a temperature of 350° C. the thermal decomposition reactions are inappreciable, the two reactions

$$Ca(OH)_2 + 2CH_3Cl = 2CH_3OH + CaCl_2 \qquad (3)$$
$$Ca(OH)_2 + 2CH_3Cl + 2CH_3OH = 2(CH_3)_2O + 2H_2O + CaCl_2 \qquad (10)$$

occur alone in the reaction chamber, and it is possible to compare the experimental results obtained with those which this set of reactions should give.

The application of Nernst's theorem gave as the points of equilibria of these equations:

$$K_3 = \frac{CH_3OH}{CH_3Cl} = 50 \text{ (approx.)}$$

$$K_{10} = \frac{(CH_3)_2O \times H_2O}{(CH_3Cl \times CH_3OH)} = 250 \text{ (approx.)}$$

If it is assumed that these values are correct, and if it is further assumed that equilibrium is established in the reaction chamber, then the following reactions obtain:

Let y = partial pressure in atmosphere of H_2O in initial H_2O-CH_3Cl mixture

Then $1 - y$ = partial pressure in atmosphere of CH_3Cl in initial H_2O-CH_3Cl mixture

Let x = partial pressure in atmosphere of $(CH_3)_2O$ at equilibrium

$y + x$ = partial pressure in atmosphere of H_2O at equilibrium

$\sqrt{\frac{x(x+y)}{K_3K_{10}}}$ = partial pressure in atmosphere of CH_3Cl at equilibrium

$K_3\sqrt{\frac{x(x+y)}{K_3K_{10}}}$ = partial pressure in atmosphere of CH_3OH at equilibrium

$$\text{Then } x + (y + x) + K_3\sqrt{\frac{x(x+y)}{K_3K_{10}}} + \sqrt{\frac{x(x+y)}{K_3K_{10}}} = 1 \qquad (a)$$

$$\text{or } 1 - 4x - 2y + 4x^2 + 4xy + 4y^2 = \frac{(1+K_3)}{K_3K_{10}}(x^2 + xy) \qquad (b)$$

Now, from calculated values of K_3 and K_{10},

$$\frac{(1+K_3)^2}{K_3K_{10}} = 0.21$$

$$\text{Therefore,} \quad 1 - 4x - 2y + 3.79xy + y^2 = 0$$

From this equation the partial pressure of methyl ether resulting from any initial partial pressure of water can be computed, assuming equilibrium is reached. Now, evidently,

$$(1 - y) - \sqrt{\frac{x^2 + xy}{K_3K_{10}}} = \text{partial pressure of methyl chloride}$$

used. Therefore, if x' = per cent yield as methyl ether, it follows

$$x' = \frac{2x}{(1 - y) - \sqrt{\frac{x^2 + xy}{K_3K_{10}}}} \qquad (c)$$

where x is obtained from Equation *b*.

Equation *c* is plotted as Curve 14*A*, while the results obtained experimentally are plotted as Curve 14*C*. Although the curves are obviously related, the agreement between the two is not good. When it is considered, however, that Reaction 10 is consecutive to Reaction 3, and, moreover, that the former is far more complex than the latter, requiring as it does the fortuitous juxtaposition of a molecule of methanol with one of methyl chloride and one of calcium hydroxide, it is hardly to be expected that under the conditions existing in the reaction chamber Reaction 10 will approach equilibrium as closely as will Reaction 3. On this assumption it follows:

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[10] Curves 12*B* and 12*C* were plotted on the assumption that all the methane obtained was caused by the decomposition of methyl chloride according to the reaction found experimentally:

$$2CH_3Cl = C + CH_4 + 2HCl$$

If a = extent to which Reaction 3 approaches equilibrium,
and e = extent to which Reaction 10 approaches equilibrium, *relative* to Reaction 3, then the term

$$\frac{(1 + K_3)^2}{K_3K_{10}} \text{ becomes } \frac{(1 + aK_3)^2}{eaK_3K_{10}} = \frac{(aK_3)^2}{eaK_3K_{10}} = \frac{aK_3}{eK_{10}}$$

on the assumption that aK_3 is large with respect to 1. This assumption is certainly true, because from the curve for Run 4 it is seen that although Reaction 10 was suppressed by water vapor, the conversion of methyl chloride is well above 90 per cent. Nernst's formula indicates that it should be 98 per cent at equilibrium; hence equilibrium is almost reached—that is, a very nearly equals 1.

Now if one assumes that the value of $\frac{a}{e} = 8$—that is, that Reaction 10 approached equilibrium only one-eighth as closely as did Reaction 3, then $\frac{(1 + K_3)^2}{K_3K_{10}} = \frac{8K_3}{K_{10}}$, approximately.

Hence, Equation 2 becomes

$$\begin{aligned} 1 - 4x - 2y + 4x^2 + 4xy + 4y^2 &= 1.60(x^2 + xy) \\ = 1 - 4x - 2y + 2.40x^2 + 2.40xy + y^2 &= 0 \qquad (b') \end{aligned}$$

Hence, Equation c becomes c':

$$x' = \frac{2x}{(1 - y) - \sqrt{\dfrac{x^2 + xy}{K_3K_{10}/8}}} \qquad (c')$$

By using Equation c' there is obtained a new set of values for x', which are plotted as Curve 14B. It is seen that this curve agrees quite well with the experimental curve.

This theoretical confirmation of the experimental results obtained indicates that the explanation advanced of the entire mechanism of the conversion of methyl chloride is at least highly probable. Moreover, it gives an additional indication of the reliability of the application of Nernst's approximation equation.

An additional effect of the presence of steam is illustrated by Curves 11 and 13. As the initial partial pressure of water vapor is increased, the extent of the conversion of calcium hydroxide to calcium chloride is decreased at any given temperature. This effect cannot be attributed to the establishment of the equilibrium[11]

$$CaCl_2 + H_2O = Ca(OH)_2 + HCl \qquad (2)$$

by the water vapor, for it was previously shown that with far higher concentrations of water vapor this hydrolysis was almost negligible.

The probable explanation is that the phenomenon is due to adsorption. Calcium hydroxide is hygroscopic at ordinary temperatures, and the formation of hydrates has also been shown[12] to take place; therefore, it is to be expected that with this pronounced secondary valence for water it will be absorbed to some extent. The effect of this absorption would be to reduce the active surface[13] of the hydroxide, which would be tantamount to a reduction of the effective volume of the latter. Since the absorption isotherm for a gas by a solid generally shows a decreasing rate of absorption as the partial pressure of the gas increases, the shape of the curve obtained is readily accounted for. On the basis of this explanation, however, since adsorption decreases with increase of temperature, Curve 13B should approach Curve 13A as the temperature increases. The experimental data are insufficient to determine whether or not this is true.

EFFECT OF INERT GAS—A knowledge of the effect on the conversion of methyl chloride of the presence of an inert gas is desirable, since the methyl chloride made commercially by the chlorination of natural gas would probably contain considerable quantities of methane. While no experimental work was carried out to determine this effect directly, it is possible to make some pertinent deductions from the results obtained using high concentrations of water vapor.

Theoretically, since there is no change of volume in the course of the reaction, the diluting effect of an inert gas can cause no displacement of the equilibrium points. The extent of the reactions therefore will not be changed. It is more difficult to predict the effect of an inert gas on the velocity of the reactions, for this velocity depends on the rapidity of diffusion of the methyl chloride into, and of the products of reaction out of, the hydroxide granules. Under fixed conditions of temperature and pressure the coefficient of diffusion of a gas will depend on the nature of the gas mixture into which it must diffuse. If the inert gas added is such that the mean free path of the molecules is increased—which would probably be the case if the diluent gas were methane—then it is to be expected that the coefficient of diffusion of the original gases will increase very slightly,[14] and hence the velocity of the reaction should increase very slightly. This is on the assumption that the adsorption of methane on the surface of the hydroxide is inappreciable. In the reaction resulting in the formation of ether the situation is more complex, since the presence of an inert gas in considerable quantities will decrease the relative number of collisions or juxtapositions of the methanol and methyl chloride molecules. As a result, therefore, the probable effect of the presence of methane will be to increase the relative velocity of Reaction 3 with respect to that of Reaction 10, and thus to favor the formation of methanol over methyl ether. In addition, since methane is a product of the thermal decomposition of the reacting materials, its presence should inhibit the decomposition.

The experimental results obtained using high partial pressures of water are in accord with these conclusions. A comparison of the curves for Runs 4 and 5 with Run 1 shows that in the presence of 0.5 atmosphere of water vapor, even though the velocity of the passage of methyl chloride through the reaction chamber is doubled thereby, the percentage absorption of methyl chloride shows no decrease. On the other hand, Curve 14C indicates by its deviation from 14B that the relative velocity of Reaction 10 has been decreased in the presence of increasing concentrations of water vapor.

STRUCTURAL CHARACTER OF CALCIUM HYDROXIDE GRANULES—Since the conversion of calcium hydroxide to calcium chloride depends upon the permeability of the hydroxide toward the gases, it is evident that the greater the porosity of the granules, the greater will be the utilization of hydroxide. Dense calcium hydroxide prepared by precipitation was found to give only one-third the yield of calcium chloride given by the hydroxide used in these experiments. No attempt was made to improve upon the character of the hydroxide used here, but undoubtedly it could be improved to a considerable extent before the porosity attained caused it to become too friable for industrial use.

EFFECT OF MATERIAL ON REACTION CHAMBER—An experimental investigation was made to determine the most advantageous material in which this reaction could be carried out on an industrial scale. Steel was first tried as the cheapest and most available material. The apparatus used was essentially that shown in Fig. 1, Part I, except that a steel tube was substituted for the glass reaction tube. A number of runs were made, and it was found that at temperatures as low as 300° C. considerable decomposition of the alcohol took place, large quantities of hydrogen and methane and some carbon monoxide being obtained. As the temperature rose this decomposition rapidly increased.

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[11] It is to be noted that experimentally it was found that one of the component reactions of Reaction 2 approached to one-eighth of the equilibrium point predicted by Nernst's formula.

[12] Kosmann, *Z. Elektrochem.*, **26**, 181 (1920).

[13] Langmuir, *Chem. News*, November 4, 1921.

[14] Meyer, "Kinetic Theory of Gases."

Copper was naturally excluded on account of its known catalytic effect on the decomposition of alcohol. Aluminium was next tried, experiments being made as in the case of steel. The results showed that the decomposition taking place in the aluminium tube under given conditions did not exceed that occurring in the glass reaction chamber.

These results agree very well with the known behavior of methanol. It has been shown[3] that on passing methanol vapor through iron tubes, it is almost entirely decomposed at 600° C. into carbon monoxide, hydrogen, and methane, while with aluminium,[3] on the other hand, no decomposition takes place even at 700° C.

Aluminium, or probably its alloys, should therefore make a satisfactory material for an industrial reaction chamber.

Conversion of Methyl Ether to Methanol

In the foregoing discussion it has been shown that the yield of methanol can be increased at the expense of the methyl ether yield by the use of steam mixed with the entering methyl chloride (Curve 10). While possessing some advantages, this employment of steam is attended by the disadvantage that it appreciably reduces the percentage utilization of the calcium hydroxide (Curve 11). An endeavor was made to avoid this difficulty by effecting the conversion of methyl chloride under anhydrous conditions and subsequently converting the ether formed into methanol by the equilibrium:

$$(CH_3)_2O + H_2O \rightleftharpoons 2CH_3OH$$

The reaction has been extensively investigated in the reverse direction. It has been shown that this decomposition of methanol is catalyzed by certain metallic oxides,[15] and a very extensive inquiry has revealed that aluminium oxide[16] is the most efficient catalyst for this decomposition. It has also been shown that water vapor will inhibit the reaction to some extent in the case of ethyl alcohol.[17] However, a search of the literature failed to reveal any data from which even an approximate indication of the point of equilibrium could be obtained. The application of Nernst's formula gave as the equilibrium point:

$$K = \frac{(CH_3OH)^2}{(CH_3)_2O \times H_2O} = 0.25$$

as shown in Part I.

The existence of so efficient a catalyst and the almost complete absence of any side reactions, together with the fact that the velocity of this reaction is almost zero below 400° C. in the absence of a catalyst, greatly simplifies the task of determining the approximate equilibrium point experimentally. Hence, since the experimental determination would, in addition to giving the desired information, serve as an excellent check on the validity of the application of Nernst's approximation formula to these reactions, it was carried out.

Experimental—The apparatus used is shown in Fig. 2. The methanol passed directly from the buret *D*, through the capillary tube into the glass reaction tube in the furnace *C*, where it vaporized, and passing over the glass beads became heated to the proper temperature. It then passed through the catalyst, which was maintained at a uniform and constant temperature. The products of reaction passed out of the reaction tube, and were collected in the tubes *A* and *B*, each containing about 20 cc. of C. P. concentrated sulfuric acid.

The aluminium oxide used as catalyst was prepared and dried exactly as described by Sabatier and Maihle.[18]

The methanol used was freshly prepared, C. P. absolute methyl alcohol, 99.5 to 100 per cent.

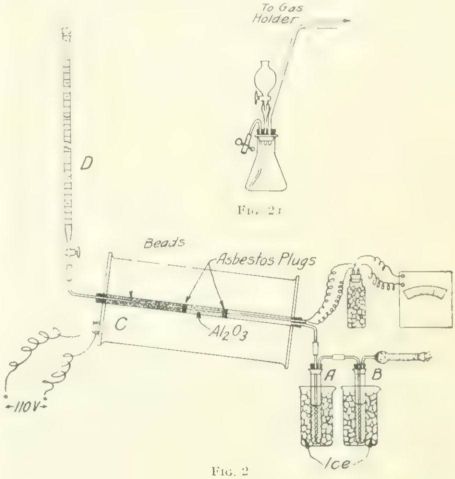

Fig. 2a

Fig. 2

Procedure—The furnace was brought to a constant temperature of 350° C., and then methanol was permitted to flow slowly into the reaction tube, generating methyl ether, until the gases leaving the reaction tube were completely absorbed by concentrated sulfuric acid. In this way all the air, moisture, etc., were displaced from the reaction tube. The buret was then shut off, and when equilibrium was established in the reaction chamber (shown by the complete cessation of the flow of gases from the reaction tube), the test tubes *A* and *B* containing concentrated sulfuric acid were put in place, as shown in the figure. The reading of the buret was recorded and the methanol was again permitted to flow very slowly into the reaction tube. The reaction proceeded very smoothly, the products of reaction being collected in tube *A*. A very small amount of gas, not exceeding 10 cc., bubbled through tube *B* in the course of a run, but the increase in weight of the latter never exceeded 2 mg. This small amount of gas was doubtless hydrogen, which, it has been shown, is formed in minute amount under these conditions.

After approximately 12 to 15 cc. of alcohol had passed into the reaction tube, the buret was shut off, and the reading recorded. When equilibrium had again been established in the reaction tube the test tubes *A* and *B* were removed. The sulfuric acid solution of ether in *A* (containing also the unchanged methanol and the water formed) was transferred to a small Erlenmeyer flask (150 cc.). Tube *A* was rinsed out several times with small amounts of concentrated sulfuric acid. The Erlenmeyer flask was fitted with a dropping funnel, a long delivery tube, and a third tube reaching to the bottom of the flask, and closed at the other end with a pinch-clamp (Fig. 2*a*). The delivery tube of the flask was connected to a 4-liter gas collection bottle, using a concentrated solution of sodium silicate as the containing fluid. Sodium silicate solution was used on account of the small solubility of methyl ether therein. The silicate solution was saturated with methyl ether.

Water was permitted to drop from the dropping funnel into the sulfuric acid solution of methyl ether in the flask, and the ether, given off at a steady rate, was collected. When about 2.5 volumes of water had been added, it was stopped, and the solution in the flask was slowly heated to gentle boiling. The delivery tube served as a reflux condenser. When the evolution of ether had ceased, the system was put under a slight pressure (1/2 inch of mercury) by siphoning a small amount of silicate solution back into the gas collection bottle. The pinch-clamp of the flask was then opened (boiling being maintained continually), and all the liquid contents of the flask were driven out. When the flask had come to room temperature, the volume of gas was read. In this way the re-solution of the liquid contents of the flask was prevented. The volume of the gas collected was corrected for pressure and temperature, and the volume of the original concentrated sulfuric acid solution of ether was added.

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[15] Grigorieff, *Bull. soc. chim.*, [3] **24**, 612 (1902); Senderens, *Ibid.*, [4] **5**, 480 (1909).

[16] Sabatier and Maihle, *Compt. rend.*, **148**, 1735 (1910); *Ann. chim. phys.*, [8] **20**, 343 (1910).

[17] Engelder, *J. Phys. Chem.*, **21**, 676 (1917).

[18] *Ann. chim. phys.*, [8] **20**, 298 (1910).

It has been shown that over 98 per cent of the methyl ether can be recovered readily from a concentrated sulfuric acid solution by adding water and heating to boiling.[19] With the precautions observed here, the recovery was probably improved.

The experimental results obtained are shown in the following table:

Table III—Conversion of Methanol to Methyl Ether

CH_3OH Delivered[a] Cc.	$(CH_3)_2O$ Received Cc.	Temperature of Catalyst ° C	Duration of Run Hrs.	$(CH_3)_2O$ per G. CH_3OH Cc.
15.07	3300	350	1:20	275
12.85	2800	350	1:00	272
13.49	2940	350	1:00	276
				Average 274

[a] All volumes are calculated to 0° C. and 760 mm

From the average of the results obtained, assuming that equilibrium was reached, the constant of equilibrium is

$$K = \frac{(CH_3OH)^2}{(CH_3)_2O \times H_2O} = \frac{[(22400/32) - (2 \times 274)]^2}{274^2} = 0.308$$

In order to verify the assumption that equilibrium was reached, the reaction was carried out in the opposite direction. To accomplish this, a known volume of pure methyl ether was displaced from a gas bottle through a humidifier maintained at 84° C. (vapor pressure of water = 380 mm.), and thence through the reaction tube to the tubes *A* and *B*. The humidifier was in principle the same as that shown in Fig. 1, but the design was modified in order to require the use of a smaller volume of water. Here also an electrically heated resistance spiral prevented the condensation of the moisture from the gas. The water used in the humidifier was previously saturated with methyl ether.

The run was carried out exactly as in the case of the reverse reaction above, except that volumes of gas in the holder were read in place of volumes of alcohol in the buret. Tube *A* was weighed before and after the run.

From the increase in weight due to the combined weight of methyl ether and water, and from the known weight of methyl ether used, the amount of water introduced was computed. It was found to be 0.995 mol per mol of methyl ether—i. e., the mixture of methyl ether and water was practically equimolecular. The results obtained are shown below:

Table IV—Conversion of Methyl Ether to Methanol

$(CH_3)_2O$ Delivered Cc	CH_3OH Recovered Cc	Temperature Catalyst ° C	Duration of Run Hrs	$(CH_3)_2O$ Converted Cc
3310	2580	350	1:10	730

The equilibrium constant, therefore, is

$$K = \frac{(CH_3OH)^2}{(CH_3)_2O \times H_2O} = \frac{(2 \times 730)^2}{2580^2} = 0.320$$

It is seen that this value agrees very well with that obtained by approaching the equilibrium from the opposite direction. Moreover, these results confirm the validity and utility of Nernst's approximation formula.

Considered from the aspect of its industrial applicability, the result obtained for the equilibrium point shows that this reaction should serve very well as a method of converting the methyl ether to methanol. In order to convert 50 per cent of the ether to methanol, 8.5 volumes of steam per volume of ether are required. However, if, as could very readily be done, the conversion is carried out in successive stages, less steam is required.

Moreover, the reaction should be very readily carried out on a large scale, for the apparatus required is simple, the velocity of reaction is very rapid, and no side reactions occur. In addition, the products are readily separated in a pure state. If the heat of the steam employed can be used in processing, the cost of conversion should be very small.

Rationale of Process

From the foregoing investigation it appears that the most advantageous method of effecting the conversion of methyl chloride to methanol is to pass the methyl chloride mixed with steam over highly porous, granular calcium hydroxide. The optimum temperature is approximately 350° C. Rates of flow considerably higher than those used in this investigation may be employed, and under these conditions the thermal decomposition of the reacting gases will probably be inappreciable (under 2 per cent at this temperature). In this way the methyl chloride can be almost quantitatively converted (98 per cent) to methanol and methyl ether. The relative amounts of the two products obtained will depend upon the relative partial pressures of the methyl chloride and steam in the initial gas mixture. Using equal partial pressures of methyl chloride and steam yields of methanol and methyl ether in the ratio 67 to 33 per cent have been obtained. However, from Curve 10 it is evident that this ratio can be readily increased by using larger proportion of steam. If, for example, the partial pressure of water compared to that of methyl chloride in the initial mixture is 3 : 1, then the resulting ratio of the yield of alcohol to ether will be 80 to 20 per cent (based on extrapolation of Curve 10). Moreover, from Curve 13 it is seen that increased concentrations of water vapor over a 1 : 1 ratio will cause no further appreciable decrease in the percentage utilization of the calcium hydroxide. However, the methyl ether can be readily converted to methanol separately, as has been shown.

If the methyl chloride employed is diluted with methane, the velocity of the reaction resulting in the production of methanol should be slightly increased, if it is affected at all. The velocity of the reaction producing methyl ether, however, will probably be sensibly decreased. In addition, the presence of methane should inhibit the thermal decomposition of the reacting gases. However, the presence of methane or any other diluent gas is objectionable because of the increased capacity of apparatus necessary to attain a given output of methanol. Moreover, the heat losses of the process will be increased, and the recovery of the products by absorption will be rendered slightly more difficult.

From an engineering aspect some considerations concerning this process may be noted. The problem of handling all materials, both reactants and resultants, should be relatively a simple one, for corrosion of pipes and containing vessels would be extremely slight. Moreover, the problem of the separation and purification of the products should give no great difficulty.

The necessity of careful temperature control is hardly a serious disadvantage, although the coefficient of heat transfer through the mass of porous granular hydroxide is quite low. Fortunately, the heat of reaction is small—only 0.45 Calories per mol of methyl chloride converted. This should greatly simplify the problem of heat transfer.

While it is not possible to give a detailed cost analysis, one can, nevertheless, obtain a rough estimate of the cost of production of methanol by this process. The largest single item in the raw materials cost is the price of chlorine. The following table gives the estimated cost of production for various prices of gaseous chlorine. Lime is taken at $10.00 per ton and natural gas of 90 per cent methane content at 10 cents per 1000 cubic feet. Steam is taken at 70 cents a ton.

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[19] Erlenmeyer and Kruchbaumer, *Ber.*, **7**, 699 (1874).

In these estimates, a yield of 70 per cent on the basis of the chlorine used is assumed for the chlorination of the methane. The hydrochloric acid produced is assumed to be recovered and is credited with its chlorine-content value. Labor and overhead are estimated at 18 cents per gallon of methanol. It may be noted that if the costs of methane, lime, and coal were all to double simultaneously, the resulting increase in the production cost of methanol would be only 7.5 cents per gallon.

TABLE IV—COST OF PRODUCTION OF METHANOL[a]

Chlorine per Lb.	Materials Cost per Gal.	Overhead and Labor per Gal.	Gross Cost per Gal.	Credit for HCl	Net Cost per Gal. CH_3OH
0.75	24.5	18.0	42.5	8.4	34.1
1.0	30.2	18.0	48.2	11.3	36.9
1.5	41.7	18.0	59.7	16.9	42.8
2.0	52.8	18.0	70.8	22.6	48.2
2.5	63.8	18.0	81.8	28.2	53.6

[a] Figures are given in cents.

A further consideration not to be overlooked is the fact that the product obtained by this process is free of acetone, which occurs as an impurity in the methanol as now manufactured. This impurity is extremely deleterious in the manufacture of formaldehyde, which is the largest single use for methanol.

The present low market price of methanol (November, 1922) is due to a temporary large oversupply. Actually, at prevailing costs of labor and wood it is very doubtful whether refined methanol can be produced at a profit for less than $1.10 per gallon. Moreover, it is not unlikely that in the near future, even with methanol at $1.25 a gallon, the owner of wood will find it more profitable to sell to the paper-pulp manufacturer, rather than to submit the wood to destructive distillation for methanol production.

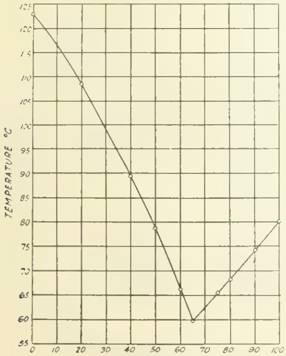
The Freezing Point-Solubility Diagram of the System TNT–Picric Acid[1,2]

By C. A. Taylor and W. H. Rinkenbach

Bureau of Mines, Pittsburgh, Pa.

Although mixtures of TNT and picric acid have been used for some time in commercial detonators and in certain types of military explosives, yet a search of the literature has failed to show any record that the nature of the system of these two compounds has been determined. Accordingly, the binary system of TNT and picric acid has been studied with a view to obtaining data that would be a contribution to the physical chemistry of explosive substances, and which might be of use in the analysis of compositions containing these bodies.

The authors have previously published a study of the binary system TNT–tetryl,[3] in which the methods used were discussed in detail. These methods were used without change in this work.



The binary system TNT-Picric acid

The TNT used was a portion of the material used in the work with tetryl previously mentioned. It was a mass of very light, fluffy, white crystals, which had not colored in the least on being kept in a dark room for six months.

The setting point was 80.27° C.

The picric acid used was purified as follows:

A very good grade of commercial picric acid was thoroughly washed five times with distilled water. It was then dissolved in hot distilled water, and the solution was filtered through paper in order to remove any insoluble matter present. The solution, on cooling, deposited the greater part of the picric acid, as very fine crystals. These were filtered off, washed several times with cold distilled water, dried on filter paper, and placed in sulfuric acid desiccators for a week before using. The product so obtained was a mass of very light, flaky crystals of a light yellow color. The setting point was found to be 121.8° C., and the melting point was found to be constant at 121.9° C. when an air-jacketed tube was used for making the determination.

Each of these compounds was fused before using in order to minimize errors in weighing.

The results obtained follow, and are shown in the form of an equilibrium diagram.

TNT %	Picric Acid %	Temperature of Extrapolated Point, ° C (Average)	Eutectic Temperature ° C (Average)
0.00	100.00	121.8	
19.97	80.03	106.7	
39.91	40.09	89.5	
49.92	50.08	78.85	
59.91	40.09	66.3	
66.30	33.70		59.8
69.80	30.20		59.4
74.76	25.24	65.35	59.8
80.01	19.99	68.4	
89.55	10.45	74.35	
100.00	0.00	80.27	

An inspection of the equilibrium diagram derived from these data shows this system to be a very simple one, no molecular compounds being formed. In order to corroborate this, melts containing different relative percentages were submitted for examination under the petrographic microscope. The materials were found to be in a very finely divided form which precluded measurement, but in each case only the two components appeared to be present.

The data furnished in this paper may be utilized for the purpose of determining the relative percentages present in unknown mixtures of these two substances. For details, the reader is referred to the paper on TNT-tetryl previously mentioned. As TNT-picric acid mixtures are not as common or important as those of TNT and tetryl, the use of this method for analytical purposes will probably not be as extensive in this case.

ACKNOWLEDGMENT

The authors gratefully acknowledge the helpful suggestions and criticisms of A. C. Fieldner, R. E. Hall, and the assistance of W. M. Myers, who examined the melts.

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[1] Received February 10, 1923.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] THIS JOURNAL, 15, 73 (1923).

Direct Determination of Dew Points of Gasoline-Air Mixtures[1]

By W. A. Gruse

Mellon Institute of Industrial Research, Pittsburgh, Pa.

A method has been devised for the direct determination of the dew points of gasoline-air mixtures in the proportions required for internal combustion engines. The method consists in blowing a fuel mixture of known composition against an internally cooled metallic mirror and observing the temperature of dew formation.

A comparison of the results obtained with those deduced from the vapor pressures of the equilibrium liquids prepared from the gasoline shows that the results directly obtained are from 15 to 20 degrees higher than those obtained indirectly.

The method is suggested as suitable for the comparison and evaluation of motor fuels.

The significance of the dew points, or temperatures of initial condensation, of motor fuels when mixed with air in the proportions employed in internal combustion engines, has been pointed out by Wilson and Barnard[2,3] and by Wilson.[4] For any one mixture of any one fuel the dew point is the lowest temperature at which the entire fuel is completely vaporized. Additional heating in the manifold is not only unnecessary, but is undesirable, since it involves a loss in volumetric efficiency. Wilson and Barnard devised an ingenious but somewhat complicated method of determining the dew point of a fuel in any air mixture desired, through measurements of the vapor pressure of the liquid in equilibrium with the completely vaporized fuel. By determining an approximate average molecular weight for the original fuel, they find it possible to calculate from the vapor pressure curve of this equilibrium liquid the temperatures, not only of initial, but also of fractional condensation of the original fuel.

The amount of work required renders the method unsuited for any but research purposes, and Wilson and Barnard were prompted to set up an arbitrary relationship for routine use. They found that the average boiling point of the equilibrium liquid was very close to the 85 per cent point on the distillation curve of the original fuel, and that by substracting a constant from this equilibrium boiling point, or from the 85 per cent point, a very close approximation to the dew point of the fuel in a certain mixture and at a given total pressure could be obtained. This relationship depends, according to these investigators, on the approximate equality of the heats of vaporization of the different paraffin hydrocarbons, determining equal rates of change of vapor pressure with temperature. It may be predicted that the relationship would not hold for aromatic and alcohol blended fuels, except as a matter of chance.

The present work is based on a belief in the fundamental significance of the dew point of a gasoline-air mixture, and has the object of devising a direct and more simple means of determining it.

Experimental

Much time and effort were spent in studying what might be called a "static" method of determining dew points. A weighed amount of gasoline was introduced into a vessel of known volume, containing dry air at a known temperature and pressure. After allowing time for the vaporization and diffusion of the gasoline, a small metallic mirror set in the wall of a metal test tube was cooled by evaporating a suitable liquid from the test tube until dew was observed on the surface of the mirror, the temperature of the mirror being known from a thermometer in the evaporating liquid. First a glass flask and then a metal vessel with glass windows, set in an air bath, were employed. Several months' experience with this method brought out a sufficient number of difficulties to cause its abandonment.

The alternate procedure was then tried—of preparing a stream of mixed air and vaporized gasoline, the composition of which could be kept constant and predetermined approximately, and blowing the mixture against a metallic mirror cooled by the method already described. The temperature of appearance of fog on the mirror and of its disappearance could then be observed. At the end of the experiment the composition was calculated from the total volumes of gasoline and air used. This method proved to be reasonably accurate.

Apparatus—The apparatus is shown in Fig. 1. Gasoline is fed from a separatory funnel, *A*, through a needle valve, *B*; drops fall regularly from a copper wire, *C*, and pass through tube *X* onto disks, *E*, made of 80-mesh copper wire gauze. Here they are met by a countercurrent stream of air, which has passed through the pressure regulator, *R* (a mercury trap device); a reservoir bottle, *P*, which equalizes the flow of air; the capillary flowmeter, *O*; the wet displacement meter, *N*;[5] and the warming coils, *S* (about 20 feet of thin metal tubing), which are immersed in the oil bath, *L*, in which the main apparatus is mounted. The temperature of the oil bath is so regulated as to effect very rapid vaporization of the gasoline; if any remains unvaporized, it will be detected in bottle *M* at the end of the runs. Failure to vaporize all the gasoline would require a repetition of the experiment at a higher bath temperature. Vaporization is entirely satisfactory with proper conditions of bath temperature and air supply. In the upper part of the vaporizing tube, *D*, above the end of tube *X*, are set three more gauze disks to prevent entrainment of unvaporized gasoline; they are entirely effective for this purpose. As an additional precaution, however, bottle *M'* is provided to receive any entrained gasoline carried through faulty operation of the device into the mixing chamber, *F*; at no time has any liquid been detected in *F* or *M'*. The mixing chamber may have a capacity of from 1 to 2 liters; a baffle, *Y*, is provided, and additional screens may be inserted to cause thorough mixing. The mixture of air and completely vaporized gasoline then passes through tube *G*, made of Pyrex glass, against a plane mirror, *S*, soldered into the wall of a copper tube, *H*. This contains a volatile liquid (chosen for the temperature it is desired to reach) in which are immersed a thermometer, *J*, graduated in tenths of degrees, and an air-jet tube, *K*. The explosive mixture is then wasted out of doors. The mirror *S* is 8 x 15 mm., and is covered with a varnish of lampblack and shellac, except for an area 3 x 5 mm. The small mirror with black edge is easier on the eye than a large mirror, and the arrangement permits a change in case one surface is injured; moreover, the large mirror is easier to solder into the copper test tube than a small one. The mirror is illuminated through a round hole, *U*, of 1-cm. diameter, cut at the level of the mirror in the wall of the bath, *L*, and is observed through another hole, *Z*, about 3 cm. in diameter and at the same level. The incandescent lamp best suited for the purpose was found to be one with a carbon filament, preferably an old smoked one or one of low power. Two mirrors were used, one of copper, gold plated, and the other of highly polished Monel metal.[6] Both tarnished to some extent. The gold mirror, on long use, seemed to suffer a curious change, indicated by the fact that the gasoline deposited in relatively large droplets, rather than in a uniform fog—in other words, it did not wet the mirror readily. Washing with the ordinary solvents and polishing with dry rouge did not alter this condition.

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[1] Presented before the Division of Petroleum Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] This Journal, **13**, 906 (1921).

[3] *J. Soc. Automotive Eng.*, **12**, 287 (1923).

[4] *Ibid.*, **10**, 6 (1922).

[5] This meter may be dispensed with and the volume of air obtained from the capillary flowmeter and the time of running. It must be removed when dew points lying below the temperature of the meter are to be determined; otherwise, a water dew point is observed.

[6] The use of Monel metal was suggested by W. S. James, of the Bureau of Standards.

In order to equalize the flow of gasoline into the vaporizing tube, a pressure greater than atmospheric by 1.5 inches of mercury was applied above it by means of a very slow stream of air which was wasted through tube *R*. With one bubble of air passing through the mercury every 5 seconds, the amount of gasoline carried away could not have been appreciable. The joint, *T*, between the funnel and the needle valve, is of the stuffing-box type, the packing being wet with litharge-glycerol mixture.

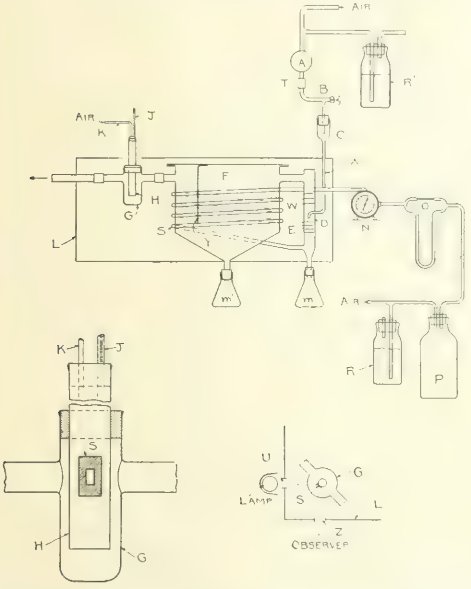

Fig. 1

Procedure—The oil bath was maintained ordinarily at 80° to 90° C. by means of an electric immersion heater; for fuels containing heavy ends a temperature of 100° to 110° C. was employed. The bath was agitated occasionally by hand, using a stirrer with a handle projecting through the bath cover. Twenty-five or 50 cc. of the gasoline, of known specific gravity, were measured into the container *A*, after filling the needle valve and the neck of the bulb *A* to a mark and working out air bubbles. The mirror was washed with acetone or ether, and polished with dry rouge on cotton wool. The copper test tube was filled with the cooling liquid to the level of the top of the mirror. This liquid soon evaporated down, leaving part of the mirror uncovered. A tendency to deposit dew more readily on the bottom of the mirror then existed, and a slight advantage was gained through a comparison of the two parts of the mirror. After setting the displacement meter at zero, and recording the time, gasoline was allowed to flow into the apparatus at a rate of 50 drops in 15 seconds. To get different mixtures this rate could be adjusted or the rate of air flow could be changed; both methods were employed. The apparatus was allowed to run 2 minutes, and then air was bubbled very slowly through the cooling liquid (for this work ethylene dichloride, b. p., 82° to 85° C., was used; it is practically noninflammable) until fog or tiny droplets were observed on the face of the mirror. By adjusting the lamp so that the image of one filament lay across the mirror, the observation was made easier. The temperature of dew formation was noted, and the mirror was allowed to warm by slowing or cutting off the current of air through the cooling liquid. The temperature of disappearance of the fog was taken, and the mean of the two temperatures regarded as the dew point. This procedure was repeated as many times as possible while the measured amount of gasoline was run through the apparatus. In order to avoid eye fatigue, one observer did not make over two or three observations, changing off with another who regulated and recorded the temperature of the mirror. Temperature changes were made very slowly, and it was often possible to observe the appearance and disappearance of fog within two or three tenths of a degree. Large ranges were, however, frequent. A moderately close and an average series are given to show the usual range of observations:

		Av		Av		Av.		Av.
Dew on	72.3	72.5	72.1	72.2	72.0	72.2	72.0	72.1
Dew off	72.7		72.3		72.4		72.2	
Average—72.2° C.								
Dew on	68.6	69.0	69.0	69.1	69.3	69.4	68.6	68.6
Dew off	69.4		69.2		69.6		68.6	
	68.3	68.4	68.7	68.7	Average 68.9° C.			
	68.6		68.8					

To eliminate personal errors and variations in mixture composition all readings were averaged.

At the end of the run the air stream through the apparatus was stopped, time noted, meter reading observed, and drainage flasks inspected for signs of incomplete vaporization. The corrected meter reading was then used for calculating the mixture composition. This mixture may be predetermined approximately, but not exactly, and the best way to compare two fuels is to make several determinations for each and plot two curves of dew point against mixture composition. Comparison of definite points can then be made.

In order to determine the accuracy of the method, the dew point of purified toluene in the mixture of 5.5 parts of air to 1 part of hydrocarbon was measured and was found to be 31.5° C. By calculation from the results of Kahlbaum on the vapor pressure of toluene, as given by Landolt-Börnstein, the dew point of a 5.5:1 air-toluene mixture is 32.3° C. It was also observed that air, approximately saturated with water at 22° C., showed a dew point of 21.2° C. The fog of water on the mirror is quite different in appearance from that of a hydrocarbon.

The following precautions are important:

1—The mirror should be cleaned before each series of observations.

2—The bath temperature should be high enough to vaporize all the gasoline; a few drops of unvaporized material may lower the dew point several degrees.

3—The rate of gasoline feed should be observed frequently and the capillary flowmeter watched for variations in air supply.

4—The outside of the tube *G* and the surface of the glass of the incandescent lamp bulb should be kept clean. Overheating the bath oil to the extent of vaporizing its light constituents should be avoided, for these condense on the tube *G*, giving a fogged appearance to the mirror.

5—A heavy dew appears only some distance below the true dew point, and will not disappear until the temperature is considerably above the true dew point.

6—One observer should not attempt to carry out the whole observation, both for the sake of accuracy in reading temperatures, and to avoid the effect of self-deception.

Results

The distillation curves of the three fuels studied are given in Fig. 2. They are commercial fuels, bought in the open market in Pittsburgh. Their differential distillation curves—percentages between 10-degree intervals—are given in Fig. 3. It will be observed from these figures that Purol (Motor) and Good Gulf have approximately the same initial and dry point, but that the former has a higher percentage of heavy naphtha fractions with a sharp increase near the end point,

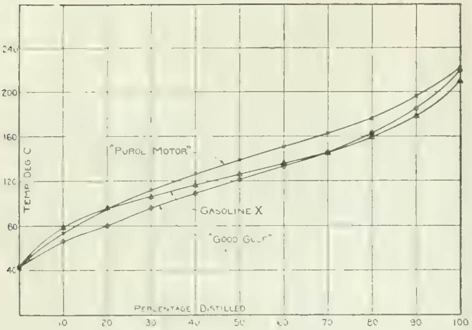

Fig. 2

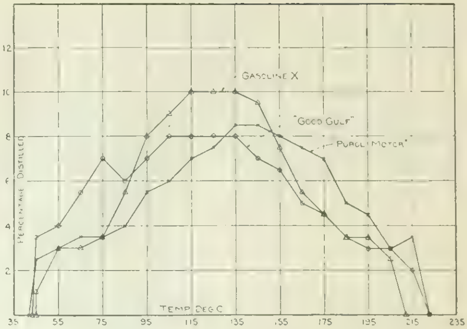

Fig. 3

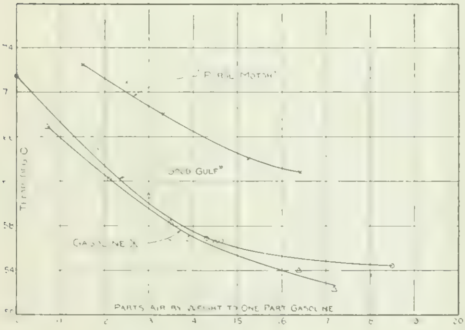

Fig. 4

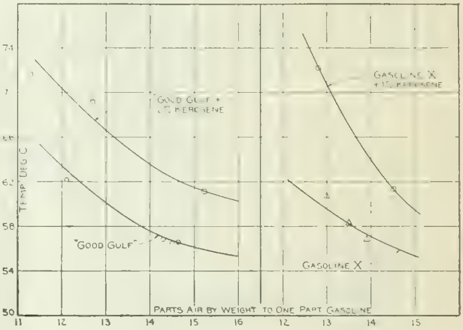

Fig. 5

while the latter has a higher percentage of light fractions, and a corresponding deficiency of heavy ends. Gasoline X is low in both light and heavy ends and much higher in middle fractions than either of the others.[7] Its initial boiling point is the same and its dry point 10 degrees lower than those of the other fuels.

The curves showing the dew points of these three gasolines for different mixture compositions are given in Fig. 4. It will be noted that Gasoline X and Good Gulf possess about the same "effective" volatility over the whole range of mixtures used in internal combustion engines, although they are strikingly different in make-up. Purol (Motor) has a much higher range of dew points, but a flatter curve; its dew point does not rise as rapidly for an enriched mixture as do the others.

In Fig. 5 are shown the effects of adding 1 and 2 per cent, respectively, of kerosene to Gasoline X and Good Gulf. The experiments were made to determine the sensitiveness of the dew point to the presence of small amounts of heavy ends. It will be seen that increases of from 4 to 6 degrees are effected, differences which can easily be detected. It will be observed also that 1 per cent of kerosene in Gasoline X seems to cause a larger increase than 2 per cent in Good Gulf. This may be due either to the points on the Good Gulf-kerosene curve being too low because of failure to vaporize small traces of the kerosene, or to the fact that Gasoline X is high in middle fractions, which, with the added kerosene, tend to run the curve up rapidly with an enriched mixture. It should be noted that dew points determined by this method might be somewhat low, because of the possibly incomplete vaporization just mentioned, but they are not likely to be too high.

Through the courtesy of D. P. Barnard and of W. S. James, samples were obtained of three of the fuels studied by Wilson and Barnard in their later work.[3] The dew points of these fuels, as directly determined, were found to be as follows:

Fuel	Mixture	Dew Point ° C.
Domestic Aviation	12:1	17
	15:1	11, approx.
Cooperative Fuel Research Gasoline A (A-2)	12:1	53.7
	15:1	51.5
D	15.4:1	Above 76
	16.4:1	74.5

Discussion

The relation of these measurements to those of Wilson and Barnard merits discussion. If the curve given by them[3] is used to find the dew points which the three fuels in the first group would have by their method, calculated from the 85 per cent point, divergences are noted, as follows:

Fuel	85% Point ° C	12:1 Calcd. ° C.	12:1 Found ° C	15:1 Calcd. ° C	15:1 Found ° C.
Gasoline X	167	38	64	33	56
Purol (Motor)	186	50	72	45	65
Good Gulf	173	42	64	37	56

It will be noted that in general their figures are somewhat over 20 degrees lower than those determined directly, and that the change in dew point corresponding to a change from a 12:1 to a 15:1 mixture is of the order of 7 or 8 degrees as measured directly, while Wilson and Barnard found a uniform difference of 4 to 5 degrees for a number of different fuels.

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[7] This gasoline was bought as a "68–70" product, but was found to have a Baumé gravity of 60.8°.

The differences are larger than the degree of accuracy indicated by Wilson and Barnard.

A comparison of the figures for the second group of fuels, studied directly by both methods, shows that direct determination gives dew points in all cases higher than those determined from the equilibrium mixture, although the differences are not quite as consistent as those shown by the first group of fuels.

Fuel	Mixture	Dew Point Indirect ° C.	Dew Point Direct ° C.
Domestic Aviation	12:1	1.0	17
	15:1	−4.0	11
Coöperative Fuel Research Gasoline			
A (A-2)	12:1	28	53.7
	15:1	24	51.5
D	12:1	66	..
	15:1	60	
	15.4:1	..	Above 75
	16.4:1	..	74.5

It may be observed that the range of temperature between the dew points at 12:1 and 15:1 varies considerably.

The possible errors of the method employed by the author are, as has been mentioned, such as to make the results obtained more probably low than high; some consistent error in the work of Wilson and Barnard, such as errors in the preparation of the equilibrium solution, which would tend to make their vapor pressure determinations too high, might account for the discrepancy.

The following features should be observed concerning the method here described:

1—The apparatus can be constructed in the ordinary laboratory and machine shop.

2—With a little practice the dew points may be read with fair accuracy and reproduciblity.

3—It is believed sufficiently direct to be free of large errors.

4—It applies to volatile fuels of any nature.

The method is offered tentatively as suitable for the direct determination of the "effective" volatility of motor fuels, with the idea that it may be useful in studying specifications and blending operations and for the control of distillation tests and other methods of evaluation.

ACKNOWLEDGMENT

The author wishes to express his gratefulness for the helpful suggestions received from W. F. Faragher, Senior Fellow, Petroleum Fellowship, Mellon Institute, and also to S. P. Marley for assistance in the construction of the apparatus used, and to S. P. Marley and R. W. Henry, for assistance in making observations.

Determination of Phenols in Coal-Tar Oils and Crude Carbolic Acid[1]

By J. Bennett Hill

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The various methods for determination of phenols or tar acids in coal-tar oils, such as crude carbolic acid, dip oil, coal-tar flotation oils, etc., have been investigated, special attention being given to the contraction method of Weiss, in which the contraction of the oil on extraction with caustic soda is taken as the per cent phenols. The claim that this method gives high results has been shown to be without foundation. The liberation methods, in which the tar acids are extracted from the oil with caustic soda, liberated from the carbolate with acid and measured, give high results when carefully run.

FROM time to time a great many methods have been advocated for determination of actual phenols or tar acids in coal-tar oils, such as creosote oil, dip oil, etc., and in crude carbolic acid. Where only a rough determination has been required, almost any of these methods is suitable. A demand for a greater accuracy of determination and closer check between producer and consumer is, however, frequently made, and it was to meet this demand that this investigation of some of the existing methods was made.

The successful methods for determination of phenols in oils and crude acids are all based on their solubility in soda and their extraction from the oils with a solution of sodium hydroxide. They may be divided into two main classes—first, those which use the contraction in the volume of the oil or the increase in the volume of the aqueous soda as the measure of the phenols; and second, those which liberate the phenols from the carbolate solution obtained and measure the volume of liberated acids. The first class may be called the "contraction" methods and the second class the "liberation" methods. Among the detailed methods belonging to the first class may be mentioned those of Weiss (Test H-11)[2] and of Chapin.[3] Weiss uses a simple repeated extraction of the distilled oil in a specially graduated separatory funnel and takes the contraction in volume of the oil as the volume of phenols contained in it. The method of Chapin consists of steam distillation of the original oil, a somewhat elaborate procedure for concentrating the phenols in the steam distillate into a small quantity of benzene, and final measurement by shaking with caustic soda solution and measuring the increase in volume, multiplying the result by a factor empirically determined, which happens to be the reciprocal of the specific gravity of the phenols.

Among the liberation methods are included those of Weiss[2] (Test H-12), Allen,[4] and most of the methods in use by various industrial laboratories. The methods in general differ only in detail, the liberation method of Weiss differing also from the others in that the phenols after liberation are dissolved in refined coal-tar naphtha before measurement.

It has been generally believed that the contraction method gave results higher than the correct values, and the liberation methods results lower than the actual but much closer than those obtained by the contraction methods, as is noted by Weiss in his description of the two methods. The author's experience has failed to bear out this impression, however, and it was therefore hoped that the present work would throw real light on the relative accuracies of the various methods.

Since the publication of the contraction and liberation methods of Weiss, he has found it advisable to make a few changes in the details of their operation, which he has not published. Thus, in the contraction method (H-11) where repeated extraction with 50 cc. of 10 per cent soda is recommended, it has been found simpler and safer to make in every

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[1] Received March 16, 1923.

[2] THIS JOURNAL, **10**, 913 (1918).

Bur. Animal Industry, Bull. **107.**

[4] Allen, "Commercial Organic Analysis," Vol. III, p. 375 (1909).

case three extractions with 100 cc. each of 10 per cent soda. Where the tar-acid content is above 35 per cent it has been found advisable to dilute the material with one or three parts of clean, dry kerosene so as to bring it within this limit. The result is of course multiplied by 2 or 4. In the liberation method (H-12), whereas originally extraction with 50-cc. portions of 10 per cent soda was recommended, it has been found better to make the extraction with 25-cc. portions of 15 to 20 per cent soda, in order to keep down the volume and to wash the carbolate so obtained with benzene before acidifying, thus removing the considerable quantity of oil dissolved by the stronger carbolate. The dissolved benzene is driven off by heat before liberation of the acids. The necessity for making all measurements at the same temperature has also been shown. It will readily be seen that since the coefficients of expansion of the tar oils are about 0.0007 to 0.0010, a difference of several degrees in temperature between initial and final measurements will make a very considerable error in the results. In the work described below, in which these methods were applied, the changes noted were used.

ANALYSES OF SYNTHETIC MIXTURES

The first part of the investigation consisted of the analyses of synthetic mixtures by the various methods. For the preparation of these mixtures a neutral coal-tar oil was used from which the phenols and pyridine bases had been completely removed by extractions with soda and with sulfuric acid. The phenols consisted of a mixture of specially purified, oil-free phenol, *o*-cresol, and *m*-*p*-cresol in proportions to approximate their natural occurrence. Mixtures of the oil and phenols were made up by volume with great care. In order to determine the effect of a less careful purification of the oil used in the mixtures, two mixtures were made from oil in which the pyridine bases were not extracted and the tar acids only roughly extracted. This showed a pyridine-base content of 4.0 per cent and a tar-acid content of 0.3 per cent, the tar acids being determined by a liberation method and being therefore actually isolated and identified as phenols. All these mixtures were analyzed by the modified Weiss contraction method, and some by the modified Weiss liberation method. The results appear in Table I.

TABLE I ANALYSES OF SYNTHETIC MIXTURE

Sample	Phenols Present Volume Per cent	Phenols Found Volume Per cent Contraction Method	Phenols Found Volume Per cent Liberation Method	Remarks
1	3.0	3.0	....	
2	20.0	20.0	20.3	
		19.8	20.2	
		20.2		
3	25.0	25.0		
4	25.0	25.2		Pyridine not extracted
5	25.2	25.2	25.9	
		25.3	26.0	
		25.5		
6	95.26	95.2		
		95.6		

It will be noted from Table I that the results with the contraction method are slightly higher than the theoretical, while the results with the liberation method are still higher. The incomplete extraction of the oil used in the mixtures appears to have very little effect on the contraction method at least.

Duplicate determinations were made by Chapin's method on the 95.26 per cent mixture corresponding to Sample 6. Although the determinations were carried out with the utmost care to avoid loss, check values of 91.0 and 91.0 per cent were obtained. It should be noted that if these results are multiplied by the specific gravity of the mixture at the temperature of measurement—in this case 1.047—values of 95.3 per cent are obtained, which check well with the theoretical. This would be the logical procedure to obtain volume per cent if Chapin's arbitrary factor were omitted.

ANALYSIS OF COMMERCIAL OIL

The fact that the contraction method gives good results on a synthetic mixture of a purified oil and a purified tar-acid mixture, does not necessarily show that it gives equally as good results on a natural coal-tar oil which has not been extracted. Accordingly, determinations were made by both the contraction and liberation methods on two samples of commercial dip oils. The results given in Table II show a good check between the two methods.

TABLE II—ANALYSES OF COMMERCIAL OILS

Sample	Phenols Found—Volume Per cent Contraction Method	Phenols Found—Volume Per cent Liberation Method
7	14.8	15.0
	15.0	15.0
8	25.6	25.4
	25.6	25.2
	25.3	...

It was noticed in the course of the work on the liberation method that in general the lower the volume of carbolate, the higher the final result. This is to be expected from the solubility of the tar acids in the sodium sulfate underlie from the liberation. For example, in the results on Sample 5 in Table I, where results were obtained which are comparatively the highest, the lowest volume of carbolate was obtained. If this method is to be used, the volume and strength of carbolate to be obtained, together with the quantity of sulfuric acid to neutralize, should be standardized.

A determination was run on Sample 8 by the liberation method but omitting the dilution of the liberated phenols with the naphtha before reading. A result of 26.5 per cent was obtained as against a mean result of 25.3 per cent obtained with the naphtha. A subsequent dilution of the phenols so obtained with naphtha precipitated out water to the extent of about 1 cc. corresponding to 1 per cent on the result. Apparently, the omission of the naphtha gives high results due to dissolved water in the phenols.

RECOMMENDED METHOD

The results of this work tend to establish the accuracy of the simple contraction method for determination of tar acids in oils and crude carbolic acid. The method is recommended for general use on coal-tar oils and crude carbolic acids in the following form:

APPARATUS—Tar-acid funnel, Type 2,[2] 200-cc. distilling flask; 100-cc. standardized pipet; condenser.

REAGENTS—Sodium hydroxide, 10 per cent solution.

PROCEDURE—A 100-cc. sample of the oil at 25° C. is measured into the distilling flask and distilled to decomposition, the distillate being collected in the tar-acid funnel. The volume of the distillate is carefully read at 25° C. and, if no solids have separated, is extracted with three successive portions of 100 cc. each of 10 per cent caustic soda solution. In each case after the soda is added to the oil, the whole is thoroughly shaken and is then allowed to settle completely before drawing off the soda layer. The volume of the residual oil after complete settling is carefully noted at 25° C. The decrease from the volume of the distilled oil before extraction to the volume after extraction is the per cent by volume of phenols.

In the case of samples containing so much naphthalene as to show separated solids at 25° C., the temperature of the three measurements may be raised to 40°, or even 60° C., extraction being made also at the same temperature.

If the sample contains over 35 per cent tar acids, the quantity taken for distillation should be cut to 50 cc. or 25 cc. so as to give not more than 35 cc. of tar acids. Before distillation the material should be made up to 100 cc. with clean, dry kerosene. The result obtained should be multiplied by 2 or 4.

Where the sample to be tested contains water it should be removed by catching the first few cubic centimeters of distillate in a small separatory funnel containing a little saturated salt solution, separating the water and adding the oil to the rest of the distillate in the tar-acid funnel.

If no diminution in volume takes place on extraction, a trace of tar acids may be detected by acidifying the soda drawn off and noting the odor.

The Vapor Pressure of Volatile Solvents[1,2]

Solutions of Benzene, Hexane, and Cyclohexane in Various Types of Lubricating Oils, with Molecular Weight Data

By Robert E. Wilson and Edward P. Wylde

Massachusetts Institute of Technology, Cambridge, Mass.

The work described in this paper was designed to determine the vapor pressure exerted by various types of volatile solvents dissolved in nonvolatile oils. The data are of particular importance in connection with (a) the recovery of solvents from gases by scrubbing with absorbent oils, (b) crank-case dilution in internal combustion engines, (c) the removal of traces of solvent from solvent-extracted edible oils.

Direct vapor pressure measurements were made on benzene, hexane, and cyclohexane (selected as typical of the three important classes of hydrocarbons), dissolved in several proportions in asphalt-base, paraffin-base, and California lubricating oils, and in various types of gas-absorbent oils. The apparatus used was similar to that previously employed by Wilson and Barnard in measuring the effective volatility of motor fuels, and while not extremely precise was quite satisfactory for the purpose on hand.

According to Raoult's law, the vapor pressure of solutions of similar molecules should be directly proportional to the mol per cent present. In order to determine whether or not this law could be relied upon as reasonably accurate for mixtures of hydrocarbon such as those studied in this paper, or to determine the direction and magnitude of the deviations therefrom, the molecular weights of the various oils used were determined by measuring the freezing-point lowering of dilute benzene solution. For oils of similar viscosity, the molecular weight increases in the following order: California, asphalt-base, paraffin-base, and vegetable or animal. The difference between the first two is slight.

The vapor pressure of most of the combinations check reasonably well with Raoult's law. The most striking exception to the rule is hexane in castor oil, which is the only combination which deviates in one direction at low concentrations and in the other at high. Benzene in castor oil and also in paraffin-base oil gives much lower vapor pressures than those calculated from Raoult's law at low molecular concentrations, but above 60 mol per cent the deviations are not large even in these cases.

In all cases increasing the temperature from 25° to 100° C. either had a negligible effect on the relative vapor pressure of the solutions or, more frequently, lowered it slightly. The effect of temperature was most pronounced on those solutions which gave vapor pressures above or near that indicated by Raoult's law, and least on those which gave the lower vapor pressures.

Hexane, which is of especial interest as representing the paraffin hydrocarbons, which constitute most of the present-day motor fuel, when dissolved in paraffin-base oil, checks Raoult's law fairly well, as might be expected from their molecular similarity. In asphalt-base oil, especially at lower temperatures, it gives abnormally high vapor pressures, indicating a lower solubility.

Benzene, probably because of its unsaturated nature, gives evidence of molecular attraction and consequent low vapor pressures, in castor, asphalt-base, and paraffin-base oil. Combining the results in this paper with those on various gas-absorbent oils, it seems that as a general rule benzene goes gradually from slight positive deviations for oils of low molecular weight to large negative deviations as the molecular weight of the oil increases.

Cyclohexane behaves very much like benzene, though giving in general slightly higher curves.

As far as deviations from Raoult's law at the lower concentrations are concerned, the four kinds of oil may be arranged in the following general order of increasing tendency to absorb, for a given molecular weight: California, asphalt-base, paraffin-base, and castor. It will be noted, however, that this is also precisely the order of increasing molecular weight for a given viscosity, and since if Raoult's law held precisely the oils of higher molecular weight would absorb less solvent, the two effects tend to neutralize one another to a surprising extent, especially for the mineral oils. The same tendency was observed in the case of the gas-absorbent oils of different molecular weight but similar source—the deviations from Raoult's law almost exactly counterbalanced differences in molecular weight. Indeed, in some ways the most striking fact brought out by the whole investigation is the comparatively small difference in the per cent by weight or volume of a given solvent absorbed under specified conditions by widely different kinds of hydrocarbon oils. This conclusion does not apply to other nonvolatile oils containing oxygen, such as glycerides, cresols, etc.

Castor oil is not completely miscible with hexane at temperatures below 48.5° C. A solubility curve is given for this combination at temperatures down to 20° C.

The method of applying the foregoing results to the three practical problems mentioned above, and some of the conclusions to be drawn from such application, are briefly discussed.

A KNOWLEDGE of the vapor pressure of volatile solvents, such as benzene and hexane, dissolved in various types of relatively nonvolatile oils, is of commercial importance in a considerable number of applications. Of these, the three most important are: (*a*) the recovery of solvents from gases by scrubbing with cold absorbent oils, as in recovering benzene from coal gas or gasoline from natural gas; (*b*) the dilution of crank-case oils with fuels in internal combustion engines; and (*c*) the removal of the last traces of volatile solvents from oils and fats obtained by solvent-extraction processes.

Furthermore, in order to be of real value, measurements should be made at a sufficient variety of different temperatures to make possible accurate inter- or extrapolations over a fairly wide temperature range.

In spite of the commercial importance of such information, very little work has been done along these lines, even at ordinary temperatures, and no generalizations have been drawn which would make it possible to calculate approximate figures for a specific case. It was the object of the investigation undertaken by this laboratory to make possible such generalizations and approximate calculations for the three general types of volatile hydrocarbons—paraffin, naphthene, and aromatic—dissolved in most of the ordinary types of nonvolatile oils. This paper deals with the general methods employed in measuring the vapor pressures and determining

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[1] Presented before the Section of Petroleum Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Published as Contribution No. 66 from the Research Laboratory of Applied Chemistry, M. I. T.

the molecular weights, and details the results on various types of lubricating oils, including castor oil. A subsequent paper covers the results on the different kinds of gas-absorbent oils.

What few data are available in the literature are discussed under the specific sections to which the data apply.

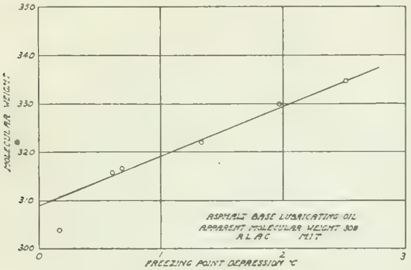

FIG 1

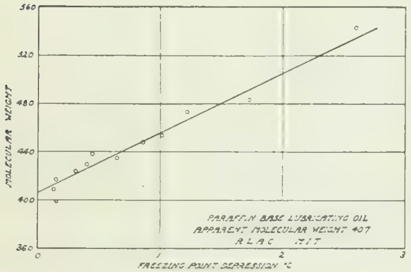

FIG 2

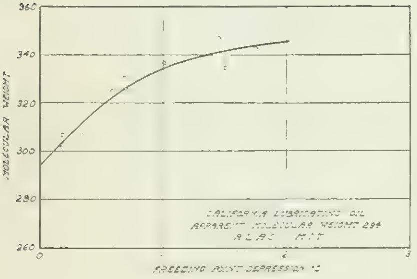

FIG 3

MOLECULAR WEIGHT DETERMINATIONS

In order to compare the observed vapor pressures of the various solutions with those calculated from Raoult's law, it is necessary to determine the average molecular weight of the various oils used, that of the volatile solvents being, of course, well known. Surprisingly little information is available along these lines, and all the determinations had to be made in this laboratory.

Vapor density methods are obviously not suitable for the determination of the molecular weights of these oils, on account of their low volatility. The simplest and most suitable method appears to be the measurement of the freezing-point lowering produced when the oils are dissolved in some pure solvent. For the purpose in hand, benzene appeared to be the most suitable solvent; since it readily dissolves practically all hydrocarbons, is easily obtainable in a fairly pure state (it need not be absolutely pure, since the freezing-point lowering is figured by difference, using the freezing point of the particular sample as the reference point), and its freezing point is very convenient (5.48° C.) for experimental manipulation. It gave excellent results with various gas-absorbent oils (molecular weights 160 to 260) and lighter lubricating oils, and was fairly satisfactory even for a paraffin-base oil (molecular weight 407). Castor oil (molecular weight 900) gave rather unsatisfactory results.[3]

The general method of determining molecular weights by the freezing point-lowering method is described in several textbooks on physical chemistry, and need not be discussed in any detail. The apparatus used was essentially the regular Beckmann arrangement, the solutions being made up by weighing the oil and then the benzene directly into the inside test tube of the apparatus. The tube is then placed inside the larger tube, which is surrounded by the ice bath, and the solution is stirred constantly. The mercury in the Beckmann thermometer falls slowly to a point slightly below the freezing point, because of supercooling, and then rises to a substantially constant level, the freezing point of the solution. This maximum constant temperature is recorded and the crystals of benzene are melted by the heat of the hand and refrozen. The two freezing points should check to 0.005 degree, and are often identical.

In the more concentrated solutions, particularly those of the heavier oils, some yellow colloidal matter slowly coagulates on standing, but does not appear to affect the results, except that it generally promotes supercooling and makes the freezing point somewhat more fugitive.

The general procedure in calculating molecular weights from data on the freezing-point lowering is to work with extremely dilute solutions and calculate the results according to the approximate formula:

$$T_0 - T = F_0 \frac{N}{N_0} = F_0 \frac{\frac{W}{M}}{\frac{W_0}{78}}$$

where

T_0 = freezing point of pure solvent
T = freezing point when containing solute
F_0 = 65.6, freezing-point constant for benzene
N = number of mols of solute
N_0 = number of mols of solvent
M = molecular weight of solute
D = $T_0 - T$ = freezing-point lowering
W = grams solute (oil)
W_0 = grams solvent (benzene)

It is the experience of the writers, however, that for work in the average laboratory the errors are diminished by making most of the measurements with concentrations high enough to give freezing-point lowerings from 0.5 to 2° C. For such fairly high concentrations this simple form of the freezing point-lowering equation is far from precise, and recourse is therefore had to a similar equation, which is somewhat more precise for higher concentrations:

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[3] When this paper was presented before the Section of Petroleum Chemistry, C. F. Mabery stated that he had not found benzene satisfactory for the determinations of molecular weights of hydrocarbons above 300 or 400, and recommended stearic acid for the purpose. The general procedure would be the same for either solvent. It is, of course, quite possible that different solvents would give somewhat different results for the molecular weights of certain oils, owing to varying degrees of association of the heavier molecules, but if all the results are calculated in terms of molecular weights *as determined in dilute benzene solution*, any deviations due to small amounts of association will merely be lumped with other causes of deviations from Raoult's law.

$$T_0 - T = F_0 \frac{N}{N + N_0} = F_0 \frac{\frac{W}{M}}{\frac{W}{M} + \frac{W_0}{78}}$$

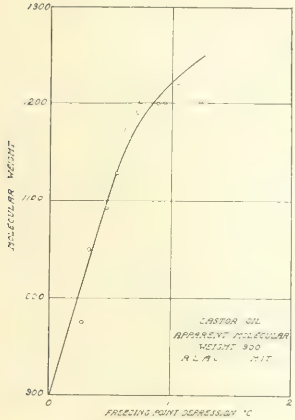


FIG. 4

Even this equation is not rigidly exact up to such high concentrations, but by plotting the values calculated for the molecular weight against the freezing-point lowering, as in the following figures, and by extrapolation of this representative line back to zero freezing-point lowering, it is possible to obtain results of sufficient accuracy for the purpose in hand, at least for hydrocarbon oils below 400 in molecular weight.

In order to check up the freezing-point constant for the sample of benzene used and the method of calculation at higher concentrations, a few determinations were made on carefully purified naphthalene, the molecular weight thus determined checking the the true value (128) within one unit.

In determining the molecular weights of various oils, it will be noted that practically all the results indicate higher apparent molecular weights at the higher concentrations. This is probably due to the tendency of some of the constituents in the oil to associate or even to form colloidal particles at the higher concentrations. This might be taken to indicate that benzene is not as good a solvent as might be desired, but it is doubtful if any solvent could be found in which the heavier molecules would not associate to some extent. The extrapolation of the line back to zero concentration should, however, eliminate most, if not all, of the error due to association.

Molecular weight determinations by the foregoing procedure have been made on thirteen different kinds of oil.[4] The results on the eight gas-absorbent oils, which check surprisingly well with their known properties, are discussed in a subsequent paper, but the curves for the four lubricating oils are shown in Figs. 1 to 4, inclusive. Of these, the results with the asphalt-base oil were quite satisfactory, while the three heavier oils gave a rather rapid change of apparent molecular weight with concentration. Although the possible error on the castor oil is rather large the figure 900 is quite reasonable, since pure ricinolein would have a molecular weight of 932 and the impurities would almost certainly lower this figure. The extrapolation to zero concentration of the curves for the other two oils gives results which are probably reliable within 2 or 3 per cent, which is sufficient for present purposes.

METHOD OF MAKING VAPOR PRESSURE MEASUREMENTS

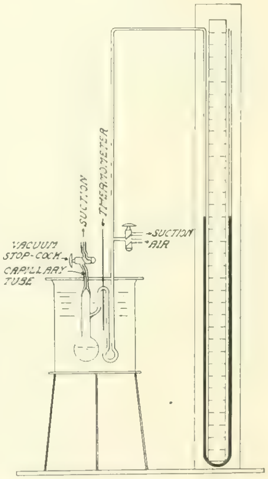
The apparatus used in making the vapor pressure measurements on the various mixtures was substantially identical with that employed by this laboratory in its investigation of the volatility of motor fuels.[5] It is shown diagrammatically in Fig. 5, and consists essentially of a 20-cc. bulb with a small balancing manometer attached, both of which are immersed in a constant temperature bath.

In adapting this apparatus and procedure to the problem in hand, it was necessary to make certain modifications. In working with gasoline the various components were not widely different in boiling point, and it was possible to remove the dissolved air by boiling off up to 1 per cent of the liquid without appreciably changing the vapor pressure of the residue. In this case, however, as much as 95 per cent of the liquid is frequently a nonvolatile oil, and boiling out the air by the previously recommended method was found to change the concentration sufficiently to make a serious error in some cases.

It was found, however, that the loss in the volatile constituent could be kept negligibly small, and yet almost completely remove the air by cooling the flask in an ice and salt bath, evacuating the air with a good vacuum pump, and then closing the stopcock, shaking, evacuating again, and repeating this procedure for five or six times until the sample ceased to give any indication of frothing or of a rise in pressure on shaking. Even then a trace of air or other fixed gas probably remained in the flask, but it did not cause appreciable error on account of the method of treating the results, described in the subsequent section.

Another precaution found necessary was in the treatment of the nonvolatile oils before the addition of the volatile solvent. Vapor pressure measurements were made on all the pure oils in the same manner as on the solutions, and a number of them, especially the vegetable oils, had vapor pressures far higher than was indicated by their boiling points. It was found that these abnormally high values were generally due to traces of moisture, and in order to decrease the magnitude of the blank correction, all the oils were heated to 125° C. and a small amount of dry nitrogen or hydrogen was bubbled through before they were used in making up the solutions. This generally reduced the vapor pressure of the oil itself to a very low figure, except in gas absorbent oil No. 8, which was quite appreciably volatile in itself.

The apparatus differs from the one previously used only in the substitution of a two-way vacuum stopcock for the three-way cock previously used, which gave some trouble on account of leakage.



APPARATUS FOR DETERMINATION OF VAPOR PRESSURES OF VOLATILE LIQUIDS

R.L.A.C. MIT

FIG. 5

All the solutions were made up by adding weighed amounts of the volatile solvent to the nonvolatile oil in 4-ounce oil sample bottles, enough being made up for at least two check determinations. About 15 cc. of the resulting solution were poured into the apparatus through the manometer arm, the whole cooled and evacuated as described above, and then the temperatures gradually raised, measurements being taken about every 10 degrees between 15° and 110° C. Before each measurement the small manometer was balanced by admitting or evacuating air from the far side, the difference between the vapor pressure of the solution and atmospheric pressure being read on the large manometer at room temperature.

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[4] Most of the determinations were made in this laboratory by D. S. Davis and F. J. Guerin as a part of their theses in fulfilment of the requirements for the degree of B.S. at M. I. T.

[5] Wilson and Barnard, THIS JOURNAL, **13**, 10, 906 (1921).

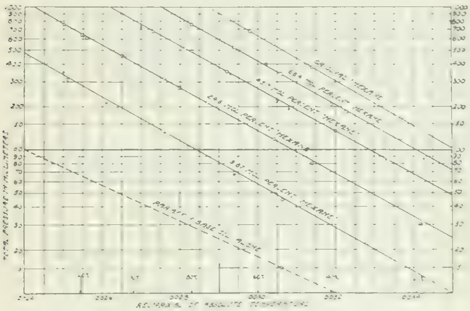

Fig. 6

Practically all the observations were made with ascending temperatures, although it is possible to check well except at the lowest temperatures if the solutions are cooled very slowly.

Method of Treating Results

If these vapor pressure observations on a given solution are plotted against the temperature, a highly curved line results, which cannot be accurately extrapolated, nor can it be used to check up the consistency of a series of observations. However, the van't Hoff equation, which may be written:

$$\frac{d \log p}{d\left(\frac{1}{T}\right)} = \frac{H}{2.3\,R}$$

indicates that if the logarithm of the vapor pressure of a pure liquid is plotted against the reciprocal of the absolute temperature, the slope of the line at a given point should be proportional to heat of vaporization at the temperature in question. For most liquids the heat of vaporization is fairly constant over a moderate range of temperatures, and this method of plotting therefore gives an approximately straight line. Similarly, in the case of a given solution a plot of the logarithm of the partial pressure of one constituent against $\frac{1}{T}$ should have a slope proportional to its heat of vaporization from that solution, which is, in turn, the algebraic sum of the heat of vaporization of the pure volatile constituent and the partial heat of dilution (mixing) at the concentration in question. For mixtures such as those under consideration in this article, the heats of mixing or dilution are, in general, quite small compared with the heat of vaporization, and the vapor pressure plots for a series of concentrations of a given volatile solvent plotted by the method recommended above should therefore give a series of approximately parallel and approximately straight lines (as, for example, in Fig. 6). This again makes possible much more accurate interpolations and extrapolations of the data, and also aids in checking up the consistency of a series of runs with varying concentrations of volatile material. For very precise work on pure compounds these approximations would not be of sufficient accuracy to be of great value, but they are extremely helpful for the purpose in hand where an accuracy of 2 or 3 per cent is quite satisfactory, especially since the measurements are made on commercial mixtures whose composition could not be precisely reproduced.

To show the precise method of treating the observations, the single series of observations on mixtures of "hexane" and paraffin-base lubricating oil will be considered in detail. Referring to Fig. 6, the upper curve plotted by the method recommended above shows the vapor pressure measurements on the "hexane"[6] itself. The four intermediate lines represent the observations on four different solutions of hexane in the paraffin-base oil, two check runs having been made on each, as indicated by the two different kinds of points.

It will be noted that all the lines for all the solutions are approximately parallel, although the blank on the oil alone has a much smaller slope, as would be expected. The agreement of the individual points is good except at the lower temperatures, where inaccuracies in reading the manometer and the presence of traces of air combine to make the results somewhat variable. Below 15° C. the readings are almost always above the extrapolated straight line, but from the laws discussed above, it is believed that a reasonable extrapolation of these lines is quite justified. Undoubtedly, however, the observed values at temperatures above 35° C. are better than those below, especially in the case of the less volatile solutions.

From these best representative lines, the total vapor pressures for the different solutions at any specified temperature may be read off and plotted as a function of concentration. The simplest method of plotting would be against the per cent by weight, but this would give highly curved lines which would require a large number of points to determine their precise location.

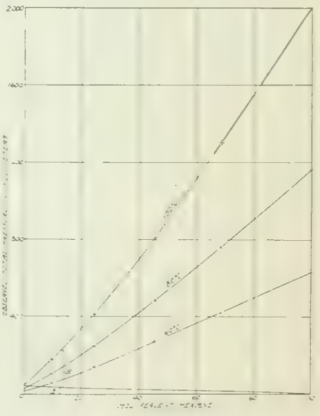

Fig. 7

According to Raoult's law, however, in "ideal" solutions—i. e., where the effective attractive forces between like and unlike molecules in the solution are identical—the par-

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[6] This material was obtained through the kindness of Thomas Midgley, Jr., of the General Motors Research Corporation, who obtained it by the fractionation of a large volume of paraffin-base gasoline. It was found, however, to have a rather wide boiling range, and was redistilled through a small laboratory column, taking only that which came over between 68° and 70° C. It was therefore not pure, and gave a vapor pressure curve slightly higher throughout than that recorded in the literature for normal hexane. The material is therefore referred to as "hexane" throughout this paper, but since all the solution vapor pressures are eventually expressed as per cent of the vapor pressure of the pure volatile constituent at the same temperature, this does not cause any appreciable error, and these *percentage* results may be applied to pure hexane.

In the case of the benzene the observed vapor pressures checked those in the literature, with a slight deviation at lower temperatures, while the curve for the cyclohexane (Eastman Kodak) checked at the boiling point although no data were found for other temperatures. The log vapor pressure *vs.* centigrade temperature curves for the three pure solvents, as well as for other related hydrocarbons, are shown in Fig. 9.

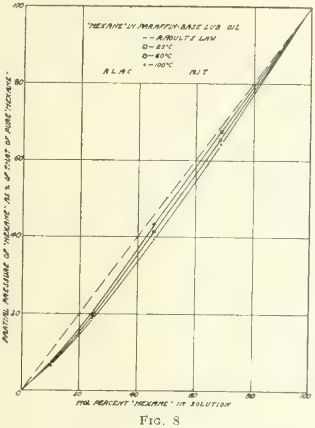

FIG. 8

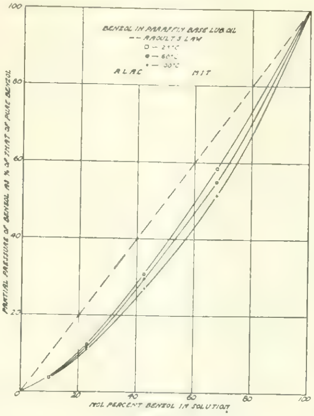

FIG. 9

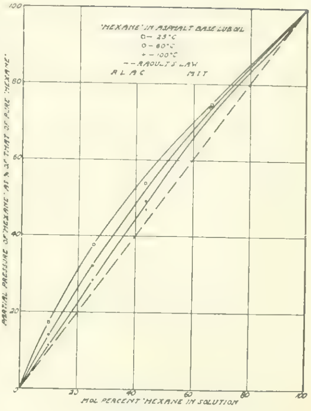

FIG. 10

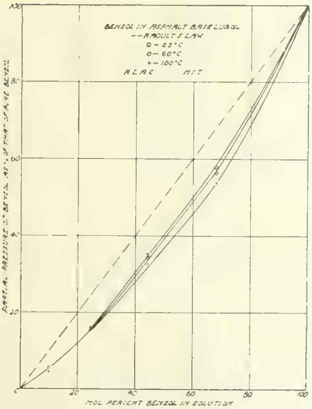

FIG. 11

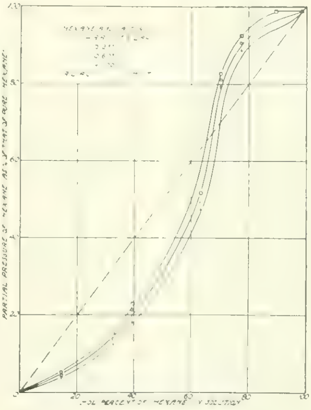

FIG. 12

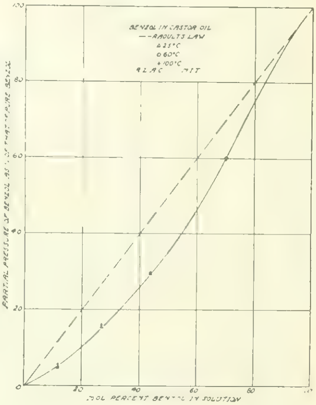

FIG. 13

tial pressure of any constituent should be directly proportional to its percentage in the solution by molecules (mol per cent). In other words, if the partial pressure of the volatile material is plotted against its mol per cent, it should give a straight line passing through the origin, and through the vapor pressure of the pure material for a mol per cent of 100.

Practically all actual solutions deviate to a greater or less extent from this ideal straight line, but the deviation for solutions of various hydrocarbons in one another should not, in general, be large. If there is a marked attractive force or tendency to form loose compounds between the solute and the solvent, the vapor pressure lowering is greater than that predicted by Raoult's law, and the lines obtained by the foregoing method of plotting would be concave upward. If, on the other hand, the two materials have comparatively little affinity for one another, as in the case of compounds which differ greatly in internal pressure, etc.,[7] the lowering of the vapor pressure would then be less than that indicated by the ideal straight line, and the curve convex upward. Sometimes this convexity is so great that the vapor pressure of certain intermediate (supersaturated) solutions is higher than that of the pure solvent, which must, of course, result in the separation of two phases between certain limits, as is illustrated by the curve for hexane in castor oil (Fig. 12).

By plotting the data from Fig. 6 in this manner, the three lines shown in Fig. 7 for 60°, 80°, and 100° C. may be obtained. It will be noted that the lines are nearly straight, but that they do not pass through the origin because the pressure measured is the total pressure (oil + hexane). To get the partial pressure of the hexane alone, a small correction term is subtracted from each observation, its magnitude being calculated on the assumption that the partial pressure of the oil itself follows Raoult's law, as indicated in the figure. This assumption may not be accurate, but the error introduced by the possible deviations is entirely negligible.

One disadvantage of the method of plotting used in Fig. 7 is the fact that the curves for the lower temperatures (25° C., etc.) cannot be read accurately, nor is extrapolation to higher or lower temperatures facilitated. If, however, the vapor pressures at the different temperatures are plotted as *per cent of the saturation pressure* of the pure volatile constituent *at the same temperature*, a great improvement results. Indeed, for all solutions obeying Raoult's law, this will give a single straight line for all temperatures, and requires only

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[7] For a good discussion of the mutual solubility of liquids see Mortimer, *J. Am. Chem. Soc.*, **44**, 1416 (1922).

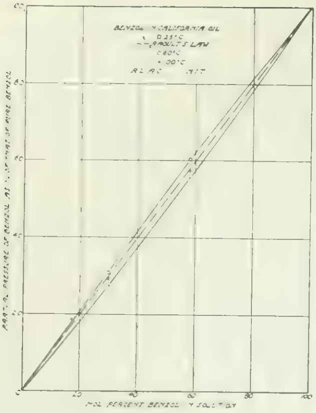

FIG. 14

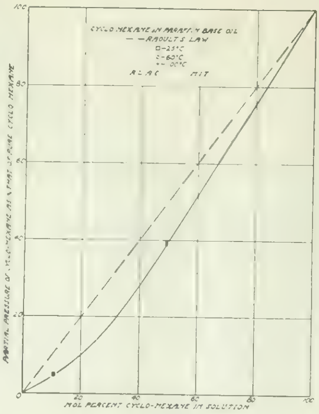

FIG. 15

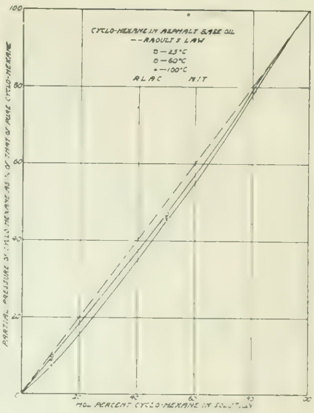

FIG. 16

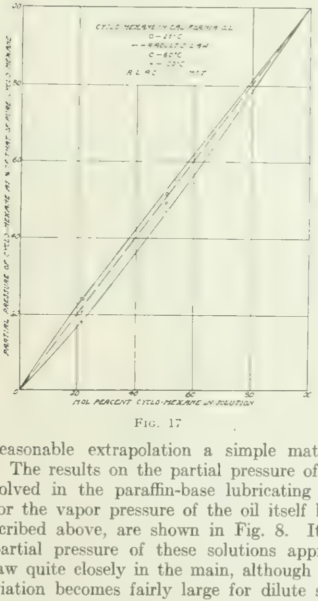

FIG. 17

a single vapor pressure-temperature curve for the pure volatile constituent in order to calculate the vapor pressure of any solution at any temperature. For solutions which deviate moderately from Raoult's law, the same method of plotting results in a family of rather closely grouped curves for the different temperatures, thus making accurate interpolation or even reasonable extrapolation a simple matter.

The results on the partial pressure of the "hexane" dissolved in the paraffin-base lubricating oil, and corrected for the vapor pressure of the oil itself by the method described above, are shown in Fig. 8. It appears that the partial pressure of these solutions approximates Raoult's law quite closely in the main, although the percentage deviation becomes fairly large for dilute solutions. The divergence between the different temperatures is little, if any, greater than the limit of error of the measurements at the lower temperatures.

It is obvious from a study of this figure that results at 0° or 200° C. could probably be calculated more accurately than they could be measured, knowing the vapor pressure curve for pure hexane. The vapor pressure *vs.* centigrade temperature curves for hexane, cyclohexane, and benzene, as well as for pentane, octane, and toluene, are shown in Fig. 21.

In the interests of economy of space, all the results obtained on the various combinations are henceforth presented in the same final form as those in Fig. 8, without presenting the intermediate stages in the graphical treatment of all the observations. The practical and theoretical significance of the results is discussed in the three following sections.

EXPERIMENTAL RESULTS

In order to have the results bear as directly as possible on the problem of crank-case dilution, three mineral oils of similar viscosity (corresponding to a light motor oil) were selected as representative of the product obtained from three different types of crude. The paraffin-base oil was made by standard refining processes from crude taken from a single well in the Appalachian field, the well being selected as one giving a very high proportion of saturated paraffins; the asphalt-base oil was similarly made from crude from a single well on the Gulf Coast, known to contain no paraffin. The California oil was obtained from the Associated Oil Company, through the kindness of C. W. Stratford, as representative of their regular product from California crude. It was known as "215 viscosity California Spindle."

The physical properties of the three samples of oil are given in the following table. The Gulf Coast and California oils are rather similar in properties, as might be expected, but the Appalachian is much lighter in gravity in spite of its higher viscosity, indicating clearly the great difference in composition. It is also interesting to note that for a given viscosity the asphalt-base oil has a lower average molecular weight than the paraffin-base oil, while the California is still a little lower. This checks up with the higher flash point of the paraffin-base oil, and the fact that fractions of a given viscosity from California crude generally have lower distillation ranges than similar fractions from Appalachian crude.

For comparative purposes the data on two straight-run, gas-absorbent oils made from Midcontinent crude are also given in the table.

TABLE I—PROPERTIES OF MINERAL OILS USED IN EXPERIMENTS

REFERRED TO AS	SOURCE	Specific Gravity 60° F.	Baumé (A. P. I. Scale)	Saybolt Viscosity at 100° F.	Flash ° F.	Fire ° F.	Av. Mol. Wt.
Paraffin-base	Appalachian crude	0.881	29.1	256	405	435	407
Asphalt-base	Gulf Coast crude	0.929	20.8	215	320	345	309
California	California crude	0.925	21.5	213	340	385	294
Gas-absorbent oil No. 2	Midcontinent	0.832	38.8	40	210	255	214
Gas-absorbent oil No. 3	Midcontinent	0.851	34.8	56	235	295	253

In addition to the mineral oils, a sample of castor oil was selected as representative of the glycerides, which are also used to a considerable extent for lubrication. Its viscosity

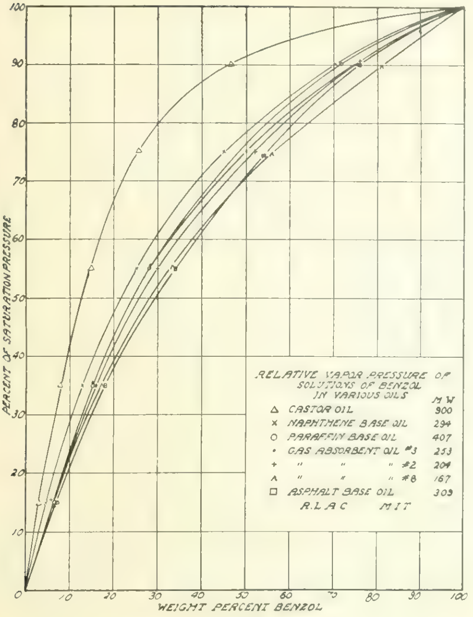

Fig. 18

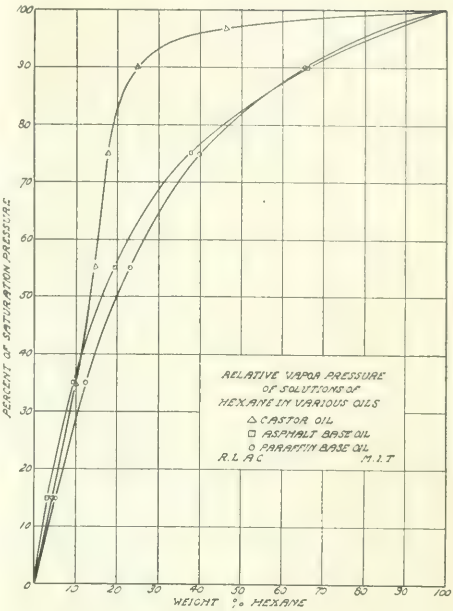

Fig. 19

and also its molecular weight were, of course, much higher than those of the mineral oils. The data obtained on it should also be applicable, at least qualitatively, to the important problem of solvent removal from solvent-extracted vegetable oils, etc.

As indicated previously, the three volatile materials—benzene, cyclohexane, and hexane—were also selected as representative of the three important classes of hydrocarbons. For convenience their physical properties are also summarized in the following table. The complete vapor pressure curves are given in Fig. 21.

MATERIAL	FORMULA	Molecular Weight	Specific Gravity 60° F.	Baumé (A. P. I.) 60° F.	Boiling Point	Viscosity at 100° F. Centipoises
Benzene	C_6H_6	78.08	0.878	29.6	79.70	0.51
Hexane	C_6H_{14}	86.15	0.660	82.9	69.05	0.72
Cyclohexane	C_6H_{12}	84.13	0.779	50.0	80.75	..

The results on ten of the twelve possible combinations between the three volatile and the four nonvolatile constituents are presented in graphical form in Figs. 8 to 17, inclusive. Of these the first six were explored rather carefully, while on the last four the shortage in available time and the apparent close agreement with Raoult's law in three of the combinations seem to justify the position of the lines as drawn, although only two sets of points were determined on each. Complete curves on three gas-absorbent oils are also given in a subsequent paper.

Rather than discuss the individual results in detail, certain general conclusions which seem to be justified by a study of the whole series of measurements will be pointed out. They should be checked by further work covering a wider range of oils. Pending the acquisition of such further data, it seems desirable to present the following as tentative conclusions based on the results to date:

1—The vapor pressures of most of the combinations check quite reasonably well with Raoult's law. The most striking exception to the rule is hexane in castor oil, which is the only combination which deviates in one direction at low concentrations and in the other at high. It is discussed in detail later. Benzene in castor oil and also in paraffin-base oil gives much lower vapor pressures than those calculated from Raoult's law at low molecular concentrations, but above 60 mol per cent the deviations are not large even in these cases.

2—In all cases increasing the temperature from 25° to 100° C. either had a negligible effect on the relative vapor pressure of the solutions, or, more frequently, lowered it slightly. The effect of temperature was most pronounced on those solutions which gave vapor pressures above or near that indicated by Raoult's law, and least on those which gave the lower vapor pressures.[8] This tendency, if extrapolated to 200° or 300° C., would seem to indicate curves concave upwards for *all* solutions at these high temperatures. This conclusion cannot be accepted without reservation, however, in view of the fact that deviations from Raoult's law generally tend to decrease as the temperature increases, but it *might* be accounted for if the apparent molecular weights determined in benzene at low temperatures tended to be high due to association which disappeared at very high temperatures.

3—Hexane, which is of especial interest as representing the paraffin hydrocarbons, which constitute most of the present-day motor fuel, when dissolved in paraffin-base oil checks Raoult's law fairly well, as might be expected from their molecular similarity. In asphalt-base oil, especially at lower temperatures, it gives abnormally high vapor pressures, indicating a lower solubility.

4—Benzene, probably because of its unsaturated nature, gives evidence of molecular attraction, and consequent low vapor pressures, in castor, asphalt-base, and paraffin-base oil. Combining the results in this paper with those in various gas-absorbent oils, it seems that as a general rule benzene goes gradually from slight, positive deviations for oils of low molecular weight to large, negative deviations as the molecular weight of the oil increases.

5—Cyclohexane behaves very much like benzene, though giving in general slightly higher curves.

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[8] For reasons discussed in connection with the methods used, the vapor pressure measurements at the lower temperatures tended to come slightly high, so that the curves for 60° and 100° C. are more reliable than those for 25° C.

6—As far as deviations from Raoult's law at the lower concentrations are concerned, the four kinds of oil may be arranged in the following general order of increasing tendency to absorb, for a given molecular weight: California, asphalt-base, paraffin-base, and castor. It will be noted, however, that this is also precisely the order of increasing molecular weight for a given viscosity, and since if Raoult's law held precisely the higher the molecular weight the lower the amount absorbed, the two effects tend to neutralize one another to a surprising extent, especially for the mineral oils. The same tendency was observed in the case of the gas-absorbent oils of different molecular weight but similar source—the deviations from Raoult's law almost exactly counterbalanced differences in molecular weight. Indeed, in some ways the most striking fact brought out by the whole investigation is the comparatively small difference in the per cent by weight or volume of a given solvent absorbed under specified conditions by widely different kinds of hydrocarbon oils. This conclusion does not, of course, apply to other nonvolatile oils containing oxygen, such as glycerides cresols, etc.

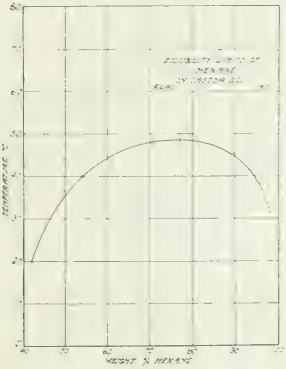

Fig. 20

Figs. 18 and 19 show the per cent by weight of benzene and hexane, respectively, held by different kinds of oil as a function of the percentage saturation in the vapor phase at 60° C. These curves are changed comparatively little by small variations in temperature, as indicated by Figs. 8 to 17, inclusive. The comparatively small proportion absorbed at low partial pressures is, of course, due to the comparatively high molecular weight of the oils as compared with the volatile constituents. It will be noted that on this basis the differences in absorptive capacity of widely different kinds of oil are surprisingly small.

Referring again to the interesting exceptional case of hexane in castor oil (Fig. 12), it will be noted that at low molecular concentrations of hexane there appears to be a surprising affinity between the two kinds of molecules, but at higher concentrations there is a marked deviation in the opposite direction—so much, indeed, that it results in the separation of two phases at lower temperatures, marked by the characteristic horizontal line on the vapor pressure curve at 25° C. The mutual solubility of the two products was determined approximately for temperatures between 20° and 50° C. by cooling various mixtures and noting the point at which two phases appeared and then redissolved on heating. The results are shown in Fig. 20. It will be noted that the two are completely miscible at temperatures above 48.5° C., while at 25° C. the two phases contain about 44 and 99 per cent hexane, respectively. These correspond to mol fractions of about 89.5 and 99.9 mols of hexane, which limits the straight line for the vapor pressure at 25° C. on Fig. 12.

Practical Aspects of the Results

For any practical problem, the general method of employing the foregoing data will be similar—for example, to determine an approximate figure for the vapor pressure of any given solution of the types discussed above at any ordinary temperature, it is merely necessary to know:

1—The approximate vapor pressure of the pure volatile constituent at the temperature in question.

2—The approximate molecular weight of the nonvolatile solvent.

3—The direction and approximate magnitude of the deviation from Raoult's law for the given type of combination at the temperature and concentration in question.

For many of the more common cases the data given in this article are sufficient to make an appropriate calculation, assuming of course that volatile paraffin hydrocarbons are typified by hexane, aromatic hydrocarbons by benzene, and naphthene hydrocarbons by cyclohexane, so far as their deviations from Raoult's law in a given solution are concerned. In many other cases it will be necessary to determine at least the molecular weight of the nonvolatile oil. Even if a given case falls outside the classes for which any data are given, the adoption of the methods of measurement and plotting described herein will greatly facilitate obtaining the desired results.

As indicated previously, the results obtained have immediate bearing on at least three important practical problems—crank-case dilution, solvent recovery by oil scrubbing, and solvent removal from extracted fats. The general application of these results to each of these cases will be discussed in brief.

Crank-Case Dilution—The dilution of oil in the crank-case of internal combustion engines by fuel which in one way or another passes the piston rings, is a well-recognized problem in many cars, especially in winter, or in tractors, etc., where kerosene is burned as the fuel.[9] How far the viscosity of the oil may be reduced by such means before trouble results is a controversial question with which this paper is not concerned, but in many cases it seems to be the limiting factor in determining the permissible volatility of the fuel for given conditions of service, and, hence, is of considerable practical importance.

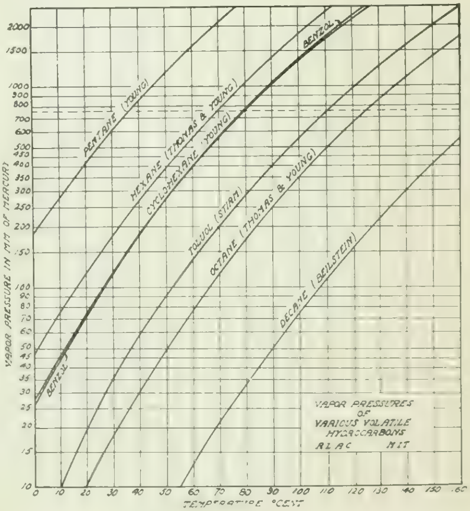

Fig 21

It might not appear at first sight that the mutual solubility of the fuel and the oil—as measured by the vapor pressure lowering produced when one is dissolved in the other—would be an important factor in crank-case dilution, but investigations of this phenomenon show that, while the degree of dilution varies greatly with temperature, fuel volatility, and engine conditions, if a given set of conditions is kept constant, the amount of fuel dissolved in the crankcase increases rapidly at first, and then the curve gradually flattens off and approaches a fairly constant degree of dilution characteristic of the particular set of conditions. This behavior can only be explained on the assumption that a point is eventually reached where the rate at which fuel is dissolving in the oil is just balanced by its rate of reëvaporation. Different oils probably differ little in the rate at which they absorb fuel initially, but they would certainly be expected to differ in the amount they take up before the partial pressure of the dissolved fuel is sufficient for it to reëvaporate at the rate necessary to prevent further dilution.

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[9] Kramer, *J. Soc. Automotive Eng.*, **6**, 335 (1920).

The foregoing results show that for given engine conditions the amount of dilution will depend upon (*a*) the boiling point of the less volatile portion of the fuel (probably best measured by the 85 per cent point), (*b*) the molecular weight of the oil, (*c*) the magnitude and direction of the deviations from Raoult's law for the combination in question.

Of these the first factor is probably the most important, but for a given gasoline (containing largely paraffin hydrocarbons) an asphalt-base oil, or a vegetable oil, will dissolve somewhat less fuel than a paraffin-base oil of similar viscosity.[10] The difference is, however, not as large as might be expected, because the difference in molecular weight tends to counterbalance the deviations from Raoult's law.

To indicate the order of magnitude of the differences between different oils, it may be stated that if a given set of engine conditions diluted a paraffin-base oil until it contained at equilibrium 15 per cent of high-gasoline ends, under similar conditions an asphalt-base oil of similar viscosity would take up about 11 per cent, and castor oil (of much higher viscosity) also about 11 per cent. A similar difference in dilution could be produced by a difference of 7° to 10° C. in the 85 per cent point of the fuel, or in the temperature of the crank-case oil, so that the differences between different kinds of oil met with in practice are by no means as important as differences likely to be encountered in fuels, and particularly in engine conditions.

To be complete, from this standpoint, the experiments should show whether or not the reduction in viscosity of the different lubricants was a function only of the amount of dilution, or varied considerably with the different kinds of oil and fuel. Unfortunately, however, the available samples of oil were practically exhausted by the vapor pressure measurements, which were more comprehensive than at first contemplated, and only a few preliminary measurements could be made. For the samples tried, it appeared that the per cent dilution was much more important than the character of the diluent or of the kind of oil, provided the latter had the same initial viscosity. For oils which differed in initial viscosity, the per cent change on dilution was, of course, greater the more viscous the oil.

For the oils used in these experiments, 15 per cent dilution with hexane or benzene gave viscosities at 100° F. between 52 and 64 seconds Saybolt.

There seemed to be no simple relationship which would permit accurate calculation of the viscosity of mixtures. Bingham's approximation[11] that fluidities are additive was found to be far from true for these cases, oils containing 15 per cent diluent giving somewhat less than half the fluidity calculated on this assumption.[12]

Solvent Recovery in Oil Scrubbers—The foregoing data are also useful in calculating approximately the equilibria involved in oil-scrubbing systems for solvent for recovery. Here the desired property is exactly the opposite from that for use in a crank-case, and a paraffin-base oil would be better as an absorbent than an asphalt-base oil of similar viscosity. Better than either would be a fraction of the lowest possible molecular weight consistent with a high enough boiling point to prevent volatilization losses in the scrubber, or contamination of the recovered product if this should be important.

A very recent paper by Cantilo[13] brings out clearly how Raoult's law may be used to calculate quantities of importance in the design of scrubbers. These calculations will be correspondingly more valuable and reliable now that the foregoing data are available as to the deviations from Raoult's law for certain typical cases.

The important case of coal-gas scrubbers for the recovery of aromatic hydrocarbons is discussed in a subsequent article.

The Removal of Solvent from Solvent-Extracted Oils—For this purpose the important part of the data is the volatility of the last traces of solvent dissolved in the vegetable oils—in other words, the slope of the vapor pressure curve as it leaves the origin. The data obtained along these lines are as yet insufficient to permit generalizations, except that the assumption of the validity of Raoult's law in this region is quite unsafe—the two values for hexane and benzene in castor oil giving about half of the theoretical vapor pressure at low concentrations.

Vapor pressure data must also be supplemented by determinations of the least amount which can be detected or is harmful in the pure oil. Complete removal is obviously impossible in any system, but it is readily possible by countercurrent steam distillation in a suitable tower to bring it below any reasonable limit set by taste, odor, or toxicity.

Acknowledgment

The writers desire to express their great indebtedness to D. S. Davis and F. J. Guerin, who made the molecular weight determinations, and to R. L. Hershey, who aided in some of the vapor pressure determinations.

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[10] In accordance with the observations of Garner as reported by Parish, *J. Am. Soc. Naval Eng.*, **32**, 57 (1920).

[11] "Fluidity and Plasticity," p. 92.

[12] Since the above was written a paper by J. L. Claydon has appeared in *Automotive Industries*, November 23, 1922, which gives some data on the effect of the amount of kerosene on the viscosity of oils. The reduction in viscosity at a given per cent dilution was considerably less than that observed with hexane and benzene, but has been checked up roughly by a few experiments with kerosene.

[13] *Can. Chem. Met.*, **6**, 177, 196 (1922).

Dr. Svedberg Honored

In recognition of his leadership as an international authority on colloid chemistry and his success in the direction of research work at the University of Wisconsin during the past semester, this university conferred the honorary degree of doctor of science upon The Svedberg, of the University of Upsala, at its June commencement. On presentation of Dr. Svedberg to the president, Prof. F. L. Paxson, chairman of the Committee on Award of Honorary Degrees, said:

> Mr. President:
>
> The Svedberg received his doctor's degree only sixteen years ago, yet to-day his laboratories in the ancient University of Upsala are recognized as the world's most active spot for the study of the formation and properties of colloids. Chemical science has advanced in those sixteen years. It has nearly revolutionized the arts of war; and the needs of war in turn have brought profound changes in the approach to chemistry. From the interactions of the two there is promise that the quiet life of mankind will forever be improved.
>
> During the past semester, as a resident in the University of Wisconsin, Professor Svedberg has brought to his department a fresh scholarship and a new technic. He has continued here that peaceful conquest of his colleagues that has marked his career in Sweden. And the results of his inspiring teaching are already to be seen in a growing disposition to look to this university as a centre for the study of the special field that he has mastered and illuminated.

Surface Tension of Alkaline Soap Solutions[1]

By E. B. Millard

Massachusetts Institute of Technology, Cambridge, Mass.

It has long been known that alkaline material increases the detergent power of soap. Salts of weak acids, which produce mild alkaline solutions upon hydrolysis, are most commonly used for this purpose. It has been found that those substances which produce the greatest decrease in surface tension are the most efficient detergents, and therefore the cleansing power of these alkaline "addition agents" can be measured in this way, as has been found by previous investigators, although their results do not in all respects agree with those of the writer.

The writer has determined the interfacial tension of various soap solutions against benzene by measuring the drop volume, comparing the ideal drop volume with such a solution, and calculating by means of the equation $2\pi\ r\ \gamma = mg$. The results show that sodium carbonate is the most effective salt for reducing surface tension.

THE use of some alkaline material in conjunction with soap in the ordinary washing of white cotton fabrics has become somewhat general practice, and long experience seems to have shown that such cleansing is done as well and more cheaply when a mild alkali is used with a diminished quantity of soap than when soap alone is employed. Silicate of soda has long been used as a builder in cake soap to make possible a larger cake of soap at a given price and as an alkaline material. Most of the substances commonly used in power laundries for this purpose are salts of weak acids—such as washing soda, borax or sodium phosphate—which by hydrolysis produce solutions of mild alkalinity and considerable reserve of alkalinity. That is, considerable unhydrolyzed salt remains in solution and this material hydrolyzes progressively as the first quantity of alkali becomes exhausted. These materials have an advantage over sodium hydroxide in that they produce far less decrease in strength of the cotton upon repeated washing.

Probably the chief function of soap in washing is that of an emulsifying agent for the greasy material which surrounds the dirt, holding it in suspension until it is removed by mechanical agitation of the solution. While the decrease in surface tension at an interface when soapy water is one of the phases is probably not an accurate or complete measure of the cleansing power of the aqueous phase, those substances which produce large decreases of surface tension when dissolved in water are probably more efficient detergents than others which have less effect upon the surface tension. The decrease in surface tension produced by an "addition agent" when a soap solution of mixed concentration is used, has been considered a measure of the cleansing power until some more definite way of measuring this property is established.[2] Interfacial tensions against benzene at 40° C. have been calculated from drop volumes measured for solutions containing 0.03 per cent of soap, together with varying concentrations of several alkaline materials which are in more or less common use in connection with soap. This soap concentration is about equal to that used in ordinary laundry practice. Some unpublished work done in the institute laboratories has shown that these benzene-soap interfacial tensions are of the same order of magnitude as when kerosene or emulsifiable oils such as olive oil are substituted for the benzene.

Previous Work

Bottazzi[3] found from his work with sodium and potassium oleates, using a stalagmometer, that pure soaps do not decrease the surface tension of water even when concentrated enough to form a skin on the surface, and that sodium or potassium hydroxide gradually decreases the surface tension. He states that only unhydrolyzed molecules of soap lower the surface tension, and that alkalies act only to diminish the hydrolysis of the soap. This conclusion is not supported by the writer's preliminary measurements of drop volumes at 25° C., in which 0.05 per cent of soap decreased the interfacial tension of water against kerosene 45 per cent, and further addition of soap caused only a slight further decrease in the surface tension, indicating an approach to surface saturation. Similar results were obtained by White and Martin[4] in connection with solutions of soap.

The measurements of Elledge and Isherwood[2] upon drop volumes of solutions of soap and salts of weak acids at 100° C. refer to concentrations of soap and added alkaline salts which are higher than those used in this work, but they show an increase in drop number (corresponding to a decrease of surface tension) upon the addition of soap alone to water. In their work no mention is made of the use of a correction curve such as those developed by Lowenstein and by Harkins, so that their drop volumes are not strictly proportional to surface tensions. These writers state that when equivalent quantities of the various addition agents are used, the same decrease in drop volume is produced regardless of the nature of the salt used. The work reported below does not agree with this conclusion; for example, the interfacial tension of 0.03 per cent soap plus 0.12 per cent $Na_3PO_4.12H_2O$ against benzene is 11.3 dynes, and the interfacial tension when 0.05 per cent sodium carbonate (an equivalent amount) is used with 0.03 per cent soap solution in place of sodium phosphate, is 14 dynes.

Shorter and Ellingworth[5] have made some experiments of a similar character, in many of which the fatty acid was in excess over total alkali. Their paper contains a full discussion of the emulsifying action of soaps.

Experimental

The apparatus used in these measurements (Fig. 1) consists of a measuring pipet sealed to a capillary tube the lower end of which is of circular cross section and ground at an angle of 90 degrees to the axis of the tube.[6] All the measurements were made with a tip having a radius of 0.343 cm. This tip is immersed in a flask of benzene supported upon a stopper having an exit for displaced air; and the whole lower portion of the apparatus is immersed in a water thermostat held at 40° C. by means of an electric heater. To the upper end of the measuring pipet is attached a small air chamber into which

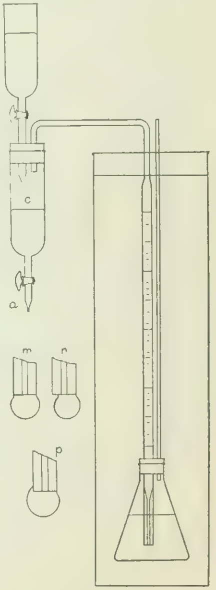

Fig. 1

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[1] Received March 9, 1923.

[2] This same assumption was adopted by Elledge and Isherwood, This Journal, **8**, 793 (1916).

[3] *Atti accad. Lincei*, **21**, II, 365 (1913). *C. A.*, **7**, 3041 (1913).

[4] *J. Phys. Chem.*, **24**, 617 (1920).

[5] *Proc. Roy. Soc. London*, **92A**, 231 (1916).

[6] The apparatus and method are adapted from Harkins and Brown, *J. Am. Chem. Soc.*, **38**, 246 (1916), as a more rapid but less accurate procedure suitable for first exploration of the field covered.

mercury can be dropped, which by displacing air causes the slow formation of drops on the end of the capillary tip. Before filling the pipet with a solution the constant temperature bath and benzene flask are set aside and the benzene is wiped from the dropping tip with a clean cloth. The tip is then immersed in the solution, which is drawn into the pipet by drawing off mercury at *a* until the meniscus stands near the top mark of the pipet. Then the tip is again wiped carefully on the sides, but not on the bottom, and mercury is allowed to flow into the air chamber *c* through a capillary nozzle controlled by stopcock *b*, until a drop of solution is suspended from the tip. This drop should wet the whole bottom of the tip and none of the side—that is, it should look like tip *m* and not like *n* or *p* of the drops sketched in the figure. In case the drop does not completely cover the circumference of the capillary, the tip must be cleaned and a perfect drop produced. Then the flask of benzene is carefully raised into position and held by the stopper while the constant temperature bath is brought up around it.

TABLE I—INTERFACIAL TENSION AGAINST BENZENE AT 40° C., TIP RADIUS 0.343

Solution: Soap %	+ Builder %		Drop Volume	Radius (Drop Volume)$^{1/3}$	Fraction of Ideal Drop	Ideal Drop Volume	Surface Tension Dynes
0.03			0.282	0.524	0.643	0.439	26.8
0.03	0.006	NaOH	0.197	0.592	0.628	0.313	19.1
0.03	0.012		0.143	0.656	0.615	0.232	14.1
0.03	0.024		0.076	0.836	0.600	0.117	7.1
0.03	0.006	Na_2CO_3	0.244	0.550	0.638	0.383	23.4
0.03	0.012		0.206	0.580	0.628	0.328	20.0
0.03	0.024		0.193	0.594	0.626	0.308	18.8
0.03	0.048		0.148	0.651	0.616	0.240	14.6
0.03	0.096		0.078	0.803	0.600	0.130	7.9
0.03	0.012	"Star" silicate	0.271	0.530	0.642	0.423	25.8
0.03	0.024		0.266	0.533	0.641	0.415	25.3
0.03	0.048		0.255	0.541	0.639	0.398	24.3
0.03	0.096		0.239	0.554	0.636	0.376	22.9
0.03	0.139		0.227	0.562	0.633	0.359	21.9
0.30	0.012	"BW" silicate	0.263	0.534	0.641	0.410	25.0
0.03	0.024		0.240	0.552	0.636	0.377	23.0
0.03	0.048		0.216	0.572	0.631	0.342	20.9
0.03	0.096		0.191	0.596	0.626	0.305	18.6
0.03	0.030	$Na_3PO_4.12H_2O$	0.206	0.582	0.629	0.327	20.0
0.03	0.060		0.171	0.618	0.622	0.275	16.8
0.03	0.090		0.138	0.664	0.616	0.225	13.7
0.03	0.120		0.114	0.708	0.608	0.187	11.4
0.03	0.06	Modified soda	0.230	0.560	0.634	0.363	22.1
0.03	0.12		0.220	0.568	0.632	0.348	21.2

After sufficient time has elapsed so that the benzene and the tip are at 40° C., stopcock *b* is adjusted so that mercury flows into the air chamber very slowly, causing the drop on the tip to increase in size. When the drop falls off from its own weight, the stopcock is closed quickly and the position of the meniscus is read. Then drops are caused to fall very slowly and they are counted until 10 or 20 have fallen, when the stopcock is closed quickly and the volume read again. As only 3 or 4 drops fall per minute a slight variation in the nearly uniform reaction time of the observer in closing the stopcock is not important, and the drop volumes obtained are substantially correct. Drop volumes so obtained are shown in Table I. The concentrations of soap and salts are in per cent by weight of the material as it is actually sold on the market, since it is these which are of primary interest to users of washing chemicals. In case a comparison of chemical equivalents is desired, these may be computed from the following data: Sodium carbonate is the C. P. calcined product; trisodiumphosphate means the hydrate $Na_3PO_4.12H_2O$; "BW" silicate of soda contains 20 per cent Na_2O, 30 per cent SiO_2, and 50 per cent water; "Star" silicate of soda contains 10.5 per cent Na_2O, and 26.7 per cent SiO_2. The "modified soda" is a mixture of equal parts of sodium carbonate and sodium bicarbonate, which approximates the composition of mixtures sold to the laundry trade but is not identical in composition with any of them, so far as the writer is aware. A good grade of commercial soap, containing 7 per cent water and free from excess alkali or fillers or builders of any kind, was used, and the solutions were freshly prepared. Mixtures of the desired compositions were obtained by diluting the proper quantities of 0.1 per cent soap solution and 0.2 per cent alkali salt to 100 cc. with distilled water. For purposes of comparison data are also included for additions of sodium hydroxide.

The ideal volume, shown in Table I, is obtained from the ratio of the tip radius to the cube root of the drop volume by means of a curve showing the measurements of Harkins and Brown,[7] and it represents the weight of the ideal drop, which is proportional to surface tension. In other words, the volume of the drop has been corrected by the use of this curve so that it corresponds to the law of Tate, and the interfacial tension is proportional to the mass of the ideal drop.

Surface tensions were calculated from the ideal drop volumes by means of the equation $2\pi r \gamma = mg$, in which 2π is the circumference of the tip, γ is the surface tension, m the effective mass of the drop, and g the acceleration of gravity. The density of water at 40° C. is 0.992, that of benzene is 0.858, so that the effective mass of the drop is the product of its volume and the difference between these densities. Since these solutions were very dilute, their densities were assumed to be equal to that of water at the same temperature. Fig. 2 shows the calculated surface tensions as a function of the per cent of alkaline material added to the soap solution.

DISCUSSION

From the results of surface tension measurements shown in Fig. 2, it will be seen that, excluding sodium hydroxide, sodium carbonate is the most effective salt for reducing the surface tension. The use of sodium hydroxide is not to be recommended on account of its weakening effect upon the cotton. A modified soda, made by mixing sodium bicarbonate with sodium carbonate, is seen to be even less effective than the sodium carbonate it contains. If the function of sodium carbonate is to produce an alkaline solution, it is only to be expected that the addition of one of the products of hydrolysis would decrease the fraction hydrolyzed and decrease the alkalinity of the solution. There would appear to be no advantage in the use of mixtures of carbonate and bicarbonate if a decrease in surface tension bears any relation to the detergent value of a washing compound.

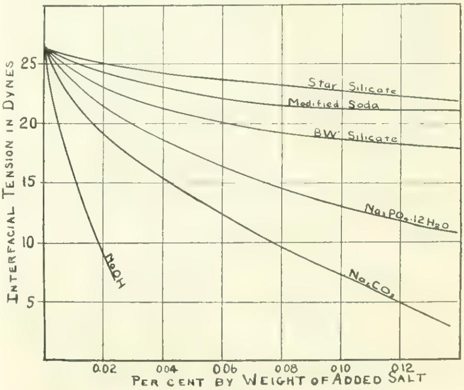

FIG. 2

From the fact that an alkaline silicate of soda produces a greater decrease of surface tension than a less alkaline silicate, a determination of the actual alkalinity or hydroxide-ion concentration of these solutions as a function of the surface tension would be of great interest. Such experiments are in progress in another laboratory in the institute. Experiments upon the effect of mixtures of soap and sodium carbonate on repeated washing of cotton cloth are also in progress.

[7] *J. Am. Chem. Soc.*, **41**, 499 (1919).

The Gelatinization of Lignocellulose—I[1]

Preliminary Paper

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In the course of certain investigations it was desirable to obtain from wood, a gelatinous, structureless mass. It was found that although coniferous woods as a class attained a high degree of gelatinization on grinding for a moderate period of time in water only, the hardwoods showed practically no change under the same treatment. Bearing in mind the pronounced gelatinizing action of dilute alkalies on starch, to which the hemicelluloses have a certain resemblance, experiments were made in which wood was ground in dilute alkali, with surprising results. The alkali showed a marked peptizing action on all woods, but particularly on the hardwoods. The gelatinized lignocellulose when dried gave a dense hornlike mass. Air-dry, gelatinized aspen had a specific gravity of 1.50, while Block[4] gives 1.2 for his product.

In most of the experimental work, an ordinary earthenware ball mill was used. This simple apparatus, in view of the high degree of gelatinization obtained, forms a marked contrast to the expensive and somewhat complicated Plauson colloid mill, and offers a good example of a case where the simplicity of a phenomenon may be masked by the magnificence of the apparatus.

Some of the domestic species of woods to which the reaction has been applied are: white pine (Pinus strobus Linn.), red pine (Pinus resinosa Ait.), western red cedar (Juniperus occidentalis Hook.), Douglas fir (Pseudotsuga taxifolia Britton), redwood (Sequoia sempervirens Endl.), bald cypress (Taxodium distichum Rich.), aspen (Populus tremuloides Michx.), sugar maple (Acer saccharum Marsh.), yellow birch (Betula lutea Michx.).

The reaction has also been applied to the bark of trees and the cereal straws.

When ground with water alone the conifers as a class gelatinize much more easily than the hardwoods; when alkaline solutions are used the reverse is true. This forms another distinction between gymnosperms and angiosperms.

IT HAS been known for a long time that wood pulps which have been obtained by a raw or mild cook—e. g., Mitscherlich sulfite—gelatinize readily by mechanical methods such as beating. In the case of raw wood as a type of lignocellulose, the opinion has been held that it is capable of only slight gelatinization. Cross and Bevan[2] state: "The hydration qualities of mechanical pulp are not very great." Furthermore, Sindall[3] states: "Mechanical wood pulp *** suffers little alteration by beating and no good purpose is attained by prolonged treatment." On the other hand, it has been suspected that the superior quality of paper made from ground wood by hot grinding as compared with cold grinding is due to a superficial "hydration."

Recently, Block[4] described some of the uses of the Plauson colloid mill, briefly mentioning the gelatinization of wood, and he states that alkali may be used for peptization. The discovery of the method of gelatinization described below was made several months before the information contained in Block's paper was available, but circumstances have prevented previous publication. It will be shown that wood gelatinizes with great ease under proper conditions, giving products having physical properties almost identical with "cellulith."

Experimental

The earthenware mill used had a total capacity of 4.5 liters. The ratio of solution to wood generally employed was 1000 cc. of the former to 25 grams of the latter. With less liquid the contents in the case of some raw materials may become too viscous to grind well. As a general rule, sawdust passing a 20-mesh sieve was used and the mill was run from 24 to 48 hours.

Action of Alkali—Among the chemicals used were barium hydroxide, ammonium hydroxide, sodium carbonate, and sodium and potassium hydroxides. The caustic alkalies, such as sodium and potassium hydroxide, have the greatest peptizing power. A 2 per cent solution of ammonium hydroxide is much less effective than a 0.25 per cent solution of caustic soda, while a 1 per cent solution of sodium carbonate has less action than the ammonium hydroxide mentioned. The marked action of small amounts of absorbed caustic soda may be shown by the following experiment: Twenty-five grams of shredded aspen, the individual particles being about 1 cm. in length and 1 mm. in width, were heated to 98° C. in a 1 per cent solution of caustic soda, the solution cooled to saturate the fibers, and filtered. The wood was then placed in the ball mill with one liter of water and ground 48 hours. The resulting product was highly gelatinized. Finer material ground for 48 hours in water only showed no noticeable gelatinization. A similar experiment with white-pine sawdust showed that the wood had taken up only 2 per cent of its weight of caustic soda by this treatment.

Woods rich in resin should be given a preliminary extraction with an organic solvent, and those of high tannin content an extraction with hot water to prevent neutralization of the alkali used in grinding. A cold, 2 per cent solution of ammonia may be conveniently employed to remove resin acids, tannin, and coloring matter.

Action of Water Alone—The angiosperms gelatinize very slowly in water alone. Aspen ground for 40 hours in this medium showed very slight change, and 100 to 110 hours' grinding was necessary to attain a good state of gelatinization. The gymnosperms as a rule gelatinize quite readily, particularly the pines and spruces, but there are exceptions; western red cedar shows no apparent gelatinization in water only, but gelatinizes in alkaline solution; cypress has so far resisted gelatinization in either medium, through a wide range of experimental conditions.

Gelatinization of Bark—The gelatinization of bark may be illustrated by the following: Thirty grams of the bark of western larch (*Larix occidentalis*) passing a 40-mesh sieve were digested in the cold for 48 hours with 500 cc. of 2 per cent ammonia, filtered, washed with cold, then with hot water, and the residue ground with one liter of 1 per cent caustic soda for 72 hours. Manipulated in the usual way, the bark after drying formed a dark, hornlike mass.

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[1] Presented before the Division of Cellulose Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] "Paper Making," **1900**, p. 169.

[3] "Elementary Manual of Paper Technology," **1906**, p. 52.

[4] *Z. angew. Chem.*, **34**, 25 (1921).

GELATINIZATION OF STRAW—The cereal straws gelatinize easily and rapidly.

ACTION OF ALCOHOLIC CAUSTIC SODA—Aspen ground in a solution of 1 per cent caustic soda in 95 per cent methanol after washing with water was found to be gelatinized. To determine the effect of an anhydrous liquid, 15 grams of aspen passing a 40-mesh sieve were dried at 105° C., placed in the ball mill with 5 grams of caustic soda and 500 cc. of absolute methanol, and ground for 96 hours. The lid of the jar was provided with a rubber gasket coated with vaseline to prevent access of moisture from the air.

When the alcoholic suspension of the wood was filtered, the residue washed with alcohol and allowed to air-dry, a product was obtained that powdered easily with the fingers. When the wood washed and dried in this manner was in turn washed with water and dried, the material was not much harder. On the other hand, if the wood was washed with water after the alcohol had been filtered off and before air-drying, it became gelatinous and gave the characteristic product on drying. This indicates that gelatinization takes place in two distinct stages.

(*a*) The wood acquires a peculiar affinity for water by mechanical and possibly chemical action.

(*b*) It combines with water to produce a gelatinous product.

CAUSE OF GELATINIZATION—Until more information is available, gelatinization may be considered as resulting primarily from the hemicelluloses in the wood combined with a secondary gelatinization of the cellulose proper.

The presence of pectin in wood has not been satisfactorily shown; since only about 1.5 per cent[5] appears to be present, its effect on gelatinization could not be very great. In the filtrate obtained by grinding aspen in a one-half per cent solution of caustic soda, methyl alcohol was detected by the Denigès method as employed by von Fellenberg.[6] A very faint iodoform test was obtained which may have been due to a trace of acetone. Tutin[7] has recently shown that 0.1 *N* alkali splits off acetone as well as methanol from pectin.

Wood gum is a general term applied to the hemicelluloses, principally xylan, that are soluble in 5 per cent caustic soda. It is stated to be incompletely soluble at ordinary temperatures in caustic soda below a concentration of 2 per cent.[8] It was thought that a few determinations of the wood gum would indicate the cause of gelatinization and support the theory that the effect of the alkali on gelatinization was due to wood gum.

The material (about 3 grams) was treated in the cold with 100 cc. of 2 per cent ammonia for 24 hours. The residual wood was then filtered off, washed first with cold and then with hot water, dried, and weighed. It was then treated with 100 cc. of 5 per cent sodium hydroxide in the cold for 24 hours with frequent shaking, and washed as above.

A preliminary extraction of yellow birch (through 60 on 100 mesh) with 5 per cent caustic soda showed that the extraction was practically complete in 24 hours, since during this period the loss in weight was 26.40 per cent, and after 48 hours, 26.77 per cent. The effect of the degree of fineness is much greater, as shown by the data:

MESH	SOLUBILITY IN 2% NH_4OH Per cent	5% NaOH Per cent	Total Loss Per cent
20 on 40	6.26	16.53	22.79
40 on 60	6.24	17.43	23.67
60 on 100	6.62	18.98	25.60
Through 100	7.06	20.46	27.50

In the following table the wood gum was determined on material passing a 100-mesh sieve:

SPECIES	NH_4OH Extract Per cent	NaOH Extract Wood Gum Per cent
White pine	12.96	5.50
Sugar maple	8.44	15.22
Aspen	8.08	20.00
Yellow birch	7.06	20.46

It will be noted that the hardwoods contain from three to four times as much wood gum as the conifer, white pine.

Young wood gelatinizes more readily than old, and the rate of gelatinization, up to a certain point, increases with the temperature. Gelatinized wood appears to be only slightly affected by boiling water. Ten grams of alkaline, gelatinized aspen were filtered, suspended in 1 liter of distilled water, boiled for 1.5 hours, filtered as dry as possible by suction, and the process repeated seven times. The residue showed no noticeable decrease in gelatinization.

Dilute alkalies did not destroy the gelatinization of aspen. To determine the possible effect of removing xylan, gelatinized aspen was allowed to digest in the cold in 5 per cent caustic soda with frequent shaking for 5 days, filtered, washed first with cold then with hot water, and allowed to dry. The residue was hard and hornlike. Some of the suspension of gelatinized aspen in 5 per cent caustic soda was then boiled under a reflux condenser for 30 minutes, filtered through fine muslin, and washed as above. The residue on drying was still very hard.

Aqueous suspensions of gelatinized wood when allowed to stand exposed to the atmosphere frequently ferment. The fermentation is at first accompanied by a pleasant ethereal odor which in time becomes nauseous. The wood has then lost its power to form the characteristic hornlike masses. This action is evidently due to bacteria. The same phenomenon was recognized many years ago in the case of well-beaten pulps.

TREATMENT OF GELATINIZED WOOD—The gelatinized wood is flocculated by acidifying the alkaline solution with acetic acid. Most of the liquid can be removed more rapidly by using an ordinary funnel filter than by means of suction or centrifuging. The flocculated mass is thrown upon the filter, washed with water until neutral, and allowed to drain by gravity as long as water drips through the funnel. It is then transferred to a Büchner funnel and suction applied, pressure being applied to the mass as it shrinks from the side of the funnel. Even after prolonged suction the water content remains about 80 per cent.

If the gelatinized wood is dried at 100° C. it blisters and honeycombs. This can be overcome by drying under a vacuum or by allowing the mass to dry in the atmosphere at temperatures of 30° to 40° C. The dry material resembles horn in color and texture, and is scarcely distinguishable from the products obtained by the prolonged beating of various chemical wood pulps.

It is difficult to keep massive articles free from air holes, particularly if the gelatinized material is transferred from the funnel filter to a suction filter. The densest masses are obtained by allowing the gelatinized wood to stand in the funnel filter until it has dried to the point where it can be handled *en masse*, and allowed to dry at room temperature. Cubes 5 mm. in diameter sawed from masses dried in the same manner showed the following specific gravities: white pine, 1.44; aspen 1.50.[9] Dunlap[10] has shown that the specific gravity of wood substance is 1.54. The gelatinized wood if entirely dry and free from air should show a corresponding specific gravity.

If a neutralized suspension of gelatinized aspen is spread on a glass plate and allowed to dry at room temperature, pale yellow, translucent films are readily obtained.

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[5] Schwalbe and Becker, *Z. angew. Chem.*, **32**, 229 (1919).

[6] *Biochem. Z.*, **85**, 68 (1918).

[7] *Biochem. J.*, **15**, 494 (1921); *Biochem. Z.*, **85**, 68 (1918).

[8] Wheeler and Tollens, *Ann.*, **254**, 322 (1889).

[9] The actual specific gravity was 1.52. This particular sample contained 3.04 per cent ash, consisting mainly of silica from the ball mill, for which a correction has been made.

[10] *J. Agr. Research*, **3**, 423 (1914).

Gelatinized wood may be dehydrated and obtained in a form suitable for quantitative work by suspending it in xylol or freshly distilled turpentine and distilling until all the water has been driven off. This method may also be used for highly "hydrated" pulps. Gelatinized aspen dehydrated with turpentine in this manner, after washing with ether, was obtained as small, very porous, globular masses that easily crumpled to a powder between the fingers. The wood so treated was no longer colored red by the phloroglucin reagent, a further proof that this reaction is due to a minor constituent of the wood, which had probably been extracted by the organic solvents.

Gelatinized wood, when dried either at room temperature or by xylol, becomes irreversible. It swells appreciably in contact with water, but shows none of the original gelatinous properties.

Degree of Gelatinization—There is no simple physical or chemical method available as yet for determining the degree of gelatinization, except when the differences are very great. In the case of the sedimentation tester more and more wood passes through the screen with increase in gelatinization.

Determination of the degree of gelatinization by means of the copper number, before and after hydrolysis, was not satisfactory. This is particularly true of the hydrolyzed samples. There was not only considerable variation in duplicate determinations under the same conditions, but wide variations with the time and degree of heating. The copper numbers were not corrected for the hydrate value.

Hours Ground in Ball Mill	Copper Numbers of Gelatinized Aspen after Hydrolysis with 5 Per cent H_2SO_4			
	Direct	15 Min.	1 Hr.	2 Hr.
65	2.61	18.0	....	....
113	3.00	19.5	....	....
137	3.60 3.58	18.9	47.6	24.5

The variations in the copper numbers after hydrolysis are due to the partial decomposition of the sugars, particularly pentoses, formed on hydrolysis.

An attempt was also made to determine the degree of gelatinization by the loss of weight on heating with 5 per cent sulfuric acid. The following results were obtained with Norway pine:

Sample	Loss in Weight Per cent
Untreated sawdust through 60 on 80 mesh	19.2
Untreated sawdust through 80 mesh	20.5
Gelatinized	21.4

The loss in weight on hydrolysis was also determined on gelatinized aspen:

Hours Ground in Ball Mill	Loss in Weight Per cent
36	16.00
60	16.82

The differences, evidently due to the degree of subdivision, shown by this method are likewise too small to be of value, and the procedure would be worthless for comparing different species.

Several experiments were made to determine the amount of sugar formed by hydrolysis of gelatinized and ungelatinized wood in an autoclave using water as well as dilute sulfuric acid. After the desired pressure was reached the digester was held at this pressure for 15 minutes and then blown. The sugars formed were determined in the usual manner and calculated as dextrose.

		Sugars Formed—Norway Pine		
			Gelatinized Wood	
Cook No.	Steam Pressure Lbs.	Ordinary Wood Per cent	Without Grinding Liquor Per cent	With Grinding Liquor Per cent
1	75	2.93	1.35	1.11
2	125	6.50	4.66.	4.79
3	200	9.03	8.54	8.55
4	250	7.53	6.65	6.48

In the foregoing table only distilled water was used during grinding and for hydrolysis under pressure.

Allowing for inability to accurately control experimental conditions with the small autoclave, it was surprising to obtain lower yields of sugar from the gelatinized wood, when higher yields were to be expected.

Hydrolysis of Gelatinized Norway Pine with Sulfuric Acid

Time Min.	Steam Pressure Lbs.	Strength of Sulfuric Acid Per cent	Sugar Formed Per cent
15	115	0.25	18.00
		0.50	18.50
		1.00	19.26
		2.00	23.90
		3.00	22.50

Practically identical results were obtained with ungelatinized wood, indicating that no appreciable difference in the yield of sugars is obtainable from gelatinized and ungelatinized wood on hydrolysis with acids.

The best method so far employed for determining the degree of gelatinization for comparative purposes consisted in placing in graduated tubes equal amounts of wood in dilute suspension and comparing the amount of settling after standing 12 hours.

Color Reactions—Wood gelatinized by means of alkali, after pressing as dry as possible, is stained very weakly by the usual phloroglucin reagent, but an intense red is developed immediately on the addition of a few drops of concentrated hydrochloric acid and stirring.

It is a noteworthy fact that wood ground either in alkaline solution or water alone is stained blue instantly with zinc chloride-iodine. The blue color is quickly removed by washing with water. This test holds for all woods to which it has been applied—namely, white pine, redwood, aspen, sugar maple, and yellow birch. It is not probable that the reaction is due to starch, since, for example, wood from a yellow birch tree about one hundred years old when ground in water was readily stained blue; when the same gelatinized wood was boiled with water, the mixture allowed to settle in a test tube, and the opalescent, supernatant solution, when cold, tested with iodine-potassium iodide solution, no blue coloration developed. Thin, dry plates of aspen gelatinized in the presence of alkali, when treated with zinc chloride-iodine, showed no noticeable change for 10 or 15 minutes, then were gradually colored an intense blue-black. If the blue stain is accepted as characteristic of cellulose, the old question as to whether the cellulose and lignin are in chemical combination is raised. At first thought it might seem to indicate the absence of chemical combination, but there is no logical reason for assuming that lignocellulose itself will not stain blue under suitable conditions. Accordingly, it seems that ordinary wood is colored yellow and not blue by the Herzberg stain, for physical rather than chemical reasons.

Hygroscopicity—Thin shavings of aspen and films of gelatinized aspen were exposed to the same atmospheric conditions and then dried at 105° C. for 4 hours. The gelatinized aspen previous to conversion to films was subjected to prolonged washing to remove the sodium acetate produced by neutralization of the alkali.

	Moisture Per cent
Natural aspen	10.65
Gelatinized aspen	11.40

The gelatinized aspen is accordingly somewhat more hygroscopic than the natural wood, conforming in this respect to gelatinized cellulose.

Miscellaneous—Aspen ground with alkali in the presence of formaldehyde gave a soft and flexible product. Dry masses of gelatinized wood when subjected to distillation gave a hard, dense charcoal.

Contributions to Chemistry of Wood Cellulose[1]

III—The Acetolysis Reaction Applied to Cellulose Isolated from Commercial Species of Wood

By Louis E. Wise and Walter C. Russell

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This is a continuation of the study of the chemical properties of wood cellulose as compared with those of cotton cellulose. Cellulose isolated by the chlorination method from a number of commercial conifers and hardwoods was subjected to cold alkaline treatment. The α-celluloses thus obtained, when acetolyzed under carefully controlled conditions, yielded appreciable amounts of cellobiose octa-acetate, which varied from 24 to 33 per cent of the theoretical yield. Under similar conditions "fibersilk" (from spruce) gave 24 per cent cellobiose octa-acetate, whereas carefully purified pine cellulose prepared by the sulfate process and normal cotton cellulose yielded 33 and 34 per cent, respectively. It is evident that as far as the cellobiose reaction is concerned, wood cellulose from different sources, and that isolated by different methods from the same source behave very similarly, and that the cellobiose grouping is characteristic of all the celluloses studied.

THE importance of fundamental data relating to the chemistry of wood cellulose has been previously emphasized.[2] If such data can be obtained, new avenues in industrial research, which hitherto have been closed because of the lack of basic knowledge regarding the constitution of cellulose, would be opened up, and empirical investigations, which in the past have dominated the cellulose field, might be relegated to a subordinate position. To give a concrete example, if the cellulosic portion of shortfibered hardwoods (like maple) were identical in constitution with that of spruce, there is no *theoretical* reason why maple cellulose might not be utilized in place of the more valuable spruce cellulose in those industries which, like the fiber-silk industry, are not primarily dependent upon fiber length or fiber structure of the cellulose used.

Normal cotton cellulose is still the logical standard by which to gage celluloses obtained from other sources. It was used in our experiments. The acetolysis reaction which the writers used in their preliminary work appeared worthy of further study. This reaction, while it has very decided limitations, indicates the presence or absence of the cellobiose linking which is so characteristic of cotton cellulose. It therefore has a direct bearing on the question of the constitution of cellulose.

Quite recently Denham, by methylating cotton cellulose and hydrolyzing the product, obtained an 89 per cent yield of 2,3,6-trimethyl glucose. His results have been reported by Irvine,[3] who has made a lasting contribution to the chemistry of cotton cellulose. Sooner or later, no doubt, this method of attack will be applied to celluloses derived from various plants, with a view towards obtaining further comparative data on the similarity or dissimilarity of these celluloses. Other methods of studying the problem are in the hands of the physical chemists and physicists. The researches of Herzog and his colleagues[4] on the crystal structure of various celluloses have already been alluded to, and their real significance can only be gaged in the light of future research.

This paper records the results of the acetolysis reaction, standardized and somewhat simplified as applied to normal (or α) cellulose isolated from a number of commercial hardwoods and softwoods. These results have been compared with those obtained in the case of purified cotton cellulose. The work is an extension of that reported in an earlier communication.

Materials

Cellulose was isolated from the following species: Balsam fir (*Abies balsamea*), hemlock (*Tsuga canadensis*), and red spruce (*Picea rubens*)—all of which are imported raw materials in the sulfite pulp industry; red cedar (*Juniperus virginiana*), used in pencil manufacture and in cabinet making; sugar pine (*Pinus lambertiana*), used as finishing lumber; aspen (*Populus grandidentata*), used in soda-pulp manufacture; beech (*Fagus americana*), yellow birch (*Betula lutea*), and sugar maple (*Acer saccharum*), which are used in millwork and furniture as well as in the hardwood distillation industry; white oak (*Quercus alba*), material for furniture; and longleaf pine (*Pinus palustris*), which is now playing such a large role in the production of sulfate pulp. With the exception of the cellulose of longleaf pine (furnished by R. H. Stevens, of Joseph H. Wallace & Company, to whom grateful acknowledgment is made), the wood celluloses were isolated by a chlorination method based on the analytical procedure described by Dore[5] for the determination of cellulose in woods. Since relatively large samples of wood sawdust were used in each experiment, and since the object was to obtain a sufficient quantity of purified cellulose for further study, no attempt was made to obtain quantitative yields. In all experiments 20 to 30 grams of sawdust passing through a 20-mesh sieve were used. The coniferous woods were extracted for 6 hours with benzene and then for a like period with 95 per cent alcohol. This treatment removed oils, fats, waxes, resins, and coloring matter, all of which might cause difficulty in subsequent treatments.

Chlorination Process—The process of chlorination was carried out by passing a stream of washed chlorine, from a cylinder of chlorine, at the rate of 60 to 80 bubbles per minute over the moist sawdust contained in a 2-liter, wide-mouth bottle. The bottle was first filled with an atmosphere of chlorine. It was provided with a double-hole stopper and an inlet and outlet tube so that the material remained in a slowly moving atmosphere of chlorine during each period of chlorination. The bottle was frequently shaken and rotated during the process, but even this did not cause contact of each wood particle with chlorine during each period of chlorination because of the tendency of the particles to form small lumps. This lumping effect was especially marked during the later periods of chlorination when the material became more of a pulp. During the first four or five chlorinations the wood became a dark orange, but the darkening became less marked with subsequent chlorinations, and the sample finally remained white in the presence of chlorine gas. The chlorination periods used were 20, 15, 15, and 10 minutes in length followed by 5 or 10-minute periods until the action was complete. In general, the conifers required a greater number of chlorinations than did the hardwoods. After each chlorination the material was shaken with water in order to insure some contact of all particles with chlorine. One hundred cubic centimeters of dilute sulfurous acid (50 grams sulfur dioxide per liter) were then added as an "antichlor," and the suspension was filtered and washed with hot water until neutral to litmus. The addition of sulfurous acid caused the material to become lighter in color, thus having a bleaching effect in addition to its dechlorinating action. Filtrations throughout the procedure were made by the use of 20-inch squares of mercerized cotton. The use of cloth filters allowed a rapid filtration, and a large part of the liquid could be pressed from the material by hand. The next step in the operation was to cover the acid-free material with a 3 per cent solution of sodium sulfite in a beaker and to heat the mixture in a boiling water bath for 45 minutes. At the end of this period the residue was filtered off and washed with hot water until free from sulfite. In the case of the hardwoods the sodium sulfite solution became a dark wine color when added to the material after the first few chlorinations. With subsequent periods of chlorination this color became lighter until it finally was no longer obtained. This was taken as an indication of the complete removal of lignin, and chlorination was stopped at this point. Upon addition of the sulfite solution to the conifers after the earlier periods of chlorination the mixture became dark brown, but with subsequent chlorinations it became light brown until finally no color was obtained. This absence of color was taken as an arbitrary end point, and chlorination was then discontinued.

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[1] Presented before the Division of Cellulose Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh Pa., September 4 to 8, 1922.

[2] This Journal, **14**, 285 (1922).

[3] *J. Soc. Chem. Ind.*, **41**, 1361 (1922); *J. Chem. Soc.* (*London*), **123**, 518 (1923).

[4] *Cellulosechemie*, **2**, 101 (1921); *Z. Physik*, **3**, 196, 343 (1920).

[5] This Journal, **12**, 264 (1920).

The material resulting from the alternate chlorine and sulfite treatments is arbitrarily defined as "total cellulose." "Normal cellulose," or α-cellulose, was obtained by treating the total cellulose with 17.5 per cent sodium hydroxide solution for one-half hour, using 50 cc. of solution for each 2 grams of material. At the end of the half-hour period an equal volume of cold water was added and the suspension filtered. The material was washed with 2 to 3 liters of cold water, then with 2 liters of 10 per cent acetic acid, and finally with 2 to 3 liters of cold water. The action of the sodium hydroxide solution caused the removal of the products of oxidation by chlorine and the alkali-soluble forms of cellulose—that is, the so-called β and γ-celluloses. The normal cellulose was dried for 16 hours at 95° to 100° C., and allowed to stand in the air until it had established an equilibrium with the moisture in the air (and was air-dry). Analytical data relating to these cellulose samples are given in Table I.

TABLE I ANALYTICAL DATA ON CELLULOSES USED IN EXPERIMENTS

CELLULOSE FROM	Water Per cent	Ash Per cent	Pentosans Per cent
Pine (wood)	7.5	0.13	1.5
Balsam (wood)	7.4	0.31	1.7
Birch (wood)	8.3	0.37	3.3
Spruce (wood)	7.6	0.22	1.5
Cedar (wood)	7.7	0.17	2.0
Maple (wood)	8.0	0.32	3.3
Aspen (wood)	7.6	0.18	5.6
Hemlock (wood)	7.5	0.16	1.8
Beech (wood)	9.7	Not determined	3.2
Oak (wood)	11.2	Not determined	3.0
Cotton (normal)	5.1	0.15	1.15
Spruce (sulfite pulp)	5.4	...	1.25
Pine (sulfate pulp)	5.4	0.31	2.2
Fiber silk (spruce)	7.5	0.50	2.4

In order to avoid misinterpretation of their results, the authors wish to have it clearly understood that they do not assume α-cellulose to be a homogeneous chemical individual or that the method of isolation used is an ideal one. Any present chemical treatment leading to the removal of lignin is necessarily drastic. It is inconceivable that under these conditions the cellulose originally present in the wood remains chemically unaffected. Some of the cellulose units are probably oxidized; others no doubt are hydrolyzed, but with our modern concept of a cellulose aggregate made up of innumerable cellulose units[6] there is no reason to assume that *all these cellulose units are destroyed*. The "mercerization test" (17.5 per cent alkali treatment) removes an appreciable amount of noncellulosic material (furfural-yielding groups) originally present in the wood. It also appears to remove substances resulting from the cellulose units that were chemically altered during the chlorination process. It is also quite probable that the alkali dissolves a portion of the cellulose the surface area of which has been largely increased in the process of isolation. The α-cellulose, therefore, represents a convenient stage in the purification of cellulose, beyond which it is inadvisable or unsafe to go.

As previously mentioned, the cellulose of longleaf pine was prepared not by this method, but by the sulfate process. Mr. Stevens, who carried out the isolation and purification of this pulp in the research laboratories of Joseph H. Wallace & Co., at Stamford, Conn., states[7] that the pulp was made from pine stumps, and that the first step in the process was a sulfate cook, using 25 per cent active alkali (calculated on the basis of the bone-dry wood). The yield was low because of the very high resin content of *Pinus palustris* and also because of the drastic nature of the cook. A yield of 24.5 per cent of fairly easy bleaching pulp (not Kraft) was thus obtained. The final methods of purification of this material are not given. Analytical data are included in Table I.

The normal cotton cellulose used by the authors was purified by the method initially outlined by the Committee on Standardization of Cellulose of the Cellulose Division of the AMERICAN CHEMICAL SOCIETY. The purification is very similar to that suggested by Robinoff.[8] This material was purified and analyzed by W. Vanselow, of Syracuse University, to whom thanks are due.

Besides the celluloses mentioned, a sample of fiber silk made from Riordon pulp, obtained through the courtesy of the duPont Fibersilk Company of Buffalo, was used in one experiment.

ORIENTATING ACETOLYSIS EXPERIMENTS

In general, the technic used in carrying out these acetolysis experiments was similar to that described in a previous article.[2] Two-gram samples of air-dried normal (α) cellulose were subjected to acetolysis. The material did not dissolve in the acetolyzing mixture as readily as in the case of cotton, owing probably to its being in a more compact form and exposing less surface to the liquid. Heating at 40° to 50° C. in a water bath was resorted to in order to effect peptization. In the initial experiments the best heating conditions were found to be for 1 hour at the end of 24 hours of acetolysis and at the end of 48 hours. Later experiments, however, indicated that such heating periods could be entirely eliminated. The acetolysis mixture was allowed to stand at room temperature (about 25° C.) for 6 to 7 days. At the end of this period a crystalline mass had formed and it was treated as described in the earlier communication. The product crystallized from alcohol was filtered, dried, recrystallized from 95 per cent alcohol, and again dried for use in the melting point determinations. The yields of cellobiose octa-acetate fluctuated widely and were often far from satisfactory, probably because of the difference in the state of division of the original samples. There-

TABLE II—RESULTS OF MELTING POINT DETERMINATIONS ON SAMPLES OF CELLOBIOSE OCTA-ACETATE

SOURCE OF CELLOBIOSE	Melting Point of Crystalline Product Alone (Uncorr.) ° C.	Melting Point of Crystalline Product Mixed with Cellobiose Octa-acetate from Cotton (Uncorr.) ° C.
Balsam	227.5 to 228.5	227 to 228
Cedar	228.5	226.5
Hemlock	227	227 to 228
Pine	227 to 228.5	227 to 228
Aspen	227 to 228	227 to 228
Beech	227 to 228.5	227.5 to 228
Birch	227.5 to 228	226.5 to 227.5
Maple	227	226.5 to 227
Oak	227.5 to 229	227 to 228.5
Spruce	227 to 228	227 to 227.5
Purified cotton	227.5 to 228	
Pine sulfate pulp	226.5 to 227	226.5 to 227.5
Fiber silk	227 to 227.5	226.5 to 227.5

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[6] THIS JOURNAL, 15, 711 (1923).

[7] Private communication, July 19, 1922.

[8] "Über die Einwirkung von Waser und Natronlauge auf Baumwolle," Dissertation, Darmstadt, **1912**.

TABLE III—COMPARISON OF YIELDS OF CELLOBIOSE OBTAINED FROM CELLULOSE ISOLATED FROM VARIOUS WOODS AND COTTON

	Pine	Balsam	Birch	Spruce	Cedar	Maple	Aspen[a]	Hemlock	Beech	Oak[c]	Pine (Sulfate)	Fiber Silk	Spruce (Sulfite)	Purified Cotton[d]
Weight of air dry cellulose taken, grams	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	1.869[b]	2.000	2.000	2.000	2.000	2.000
Weight of cellulose taken (corrected for water, pentosans, and ash), grams	1.818	1.812	1.760	1.814	1.802	1.768	1.732	1.810	1.620	1.716	1.842	1.792	1.868	1.872(a) (b) 1.911(c) (d)
Yield of cellobiose octa-acetate, grams	0.980	1.008	1.036	1.039	1.010	1.080	0.864	0.935	1.114	0.922	(a)1.274 (b)1.263	0.905	(a) 1.182 (b) 1.185	(a) 1.394 (b) 1.372 (c) 1.310 (d) 1.339
Percentage of theoretical yield of octa-acetate calculated from corrected weight of cellulose	25.8	26.6	28.2	27.4	26.9	29.2	23.9	24.7	32.9	25.7	(a)33.1 (b)32.8	24.2	(a)30.3 (b)30.3	(a)35.6 (b)35.2 (c)32.8 (d)33.5

[a] Mechanical loss during crystallization of cellobiose octa-acetate. The result is therefore low

[b] Relatively smaller amounts of acetic anhydride and sulfuric acid were used in this case.

[c] No thermostat control was used in this case.

[d] (c) and (d) of this series show the effect when the thermostat control accidentally failed. For a few hours the temperature of the acetolysis mixture dropped to 14° C. (from 25° C.); otherwise, experimental conditions remained the same.

fore, in these preliminary experiments each cellulose required individual study, and the best conditions for securing prompt peptization of individual celluloses were only obtained after considerable experimentation.

MELTING POINT DETERMINATIONS—A short-stem thermometer, 200° to 250° C. range, and a concentrated sulfuric acid bath in a Thiele melting point apparatus were used in these determinations. A melting point determination was made of each crystalline product, both alone and in admixture with an equal amount of cellobiose octa-acetate obtained from cotton (m. p. 227.5° to 228° C., uncorr.). Table II shows the results of the melting point determinations.

QUANTITATIVE ACETOLYSIS EXPERIMENTS

A standardized procedure was finally adopted, which permitted us to carry out acetolysis experiments under nearly identical conditions.

Two grams of air-dried sample were put into a mixture of 8 grams of acetic anhydride (b. p. 135° to 137° C.) and 2 grams of concentrated sulfuric acid (sp. gr. 1.83) in a 125-cc. widemouth, glass-stoppered bottle. The mixture was prepared by adding the sulfuric acid to the acetic anhydride, cooled to −10° C. at such a rate that the temperature did not rise above 0° C. during the addition. During the preparation of the mixture and the addition of the sample the glass stopper was replaced by a cork stopper through which a thermometer was inserted. The sample was pressed down so as to moisten the substance thoroughly, and the mixture was then allowed to stand for at least an hour and sometimes an hour and a half in an ice bath. The glass stopper was then replaced and the bottle put into a bath kept at 25° ± 0.2° C. by means of thermostatic control, for 6 days. If the sample had not gone into solution at the end of 24 hours, it was stirred with a small glass rod, previously placed in the bottle, and frequent stirring was given until the fibers had disappeared. Crystallization began within 50 to 60 hours after placing in the bath, and at the end of the 6-day period a stiff, crystalline mass had formed. To this mass were added 6 cc. of glacial acetic acid and the mixture was warmed on a water bath (to a temperature not above 50° C.) until it could be poured from the bottle into 200 cc. of water at 0° to 10° C. The bottle was rinsed with 150 cc. of cold water and the precipitate allowed to stand in the water at 5° to 10° C. for 1 hour. It was then filtered off on a Büchner funnel, mercerized cotton being used as the filtering medium. The precipitate was washed with cold water until free from acid and sulfate when tested with litmus and barium chloride solutions, and as much water as possible was removed by suction.

Within 24 hours the material was removed from the Büchner funnel with alcohol and allowed to remain under 200 to 250 cc. of alcohol until it was convenient to recrystallize it. The first crystallization from alcohol was accomplished by dissolving the precipitate and filtering or decanting off from any undissolved portion. Crystallization was allowed to take place slowly, after which the crystals were filtered on a weighed Gooch crucible, using asbestos as the filtering medium. The filtrate was evaporated to 75 cc. and allowed to stand for 3 days at room temperature in order to obtain a second crop of crystals. The yields recorded in Table III are based on the total yields of cellobiose octa-acetate obtained under these conditions.

The tendency in the past has been to discuss alleged differences or similarities in chemical constitution of celluloses derived from different sources on the bases of analytical data. For example, certain investigators cherish the belief that if the total cellulose isolated from a wood contains a relatively large percentage of α-cellulose, whereas that prepared from another wood by a nearly identical procedure contains a much lower percentage of α-cellulose, the original celluloses in the two woods cannot be chemically identical. Similarly, a normal cellulose which retains 5 per cent of furfural-yielding material is viewed by certain experimenters as being constitutionally different from normal cellulose retaining only 1 per cent of pentosans. These differences might just as easily result from physical differences in cellulose, elaborated in the formation of the original wood. No one will controvert the fact that residues (termed "cellulose") obtained from different woods are actually not identical. On the other hand, analytical differences cannot indicate whether or not the preponderating material in each of these various residues is actually one chemical substance, and they throw no light whatsoever on the chemical constitution of the cellulose of the original wood. Methods used in technological investigations of pulp have become a fetish and the building of hypotheses regarding the constitution of cellulose on data furnished by such methods should be discouraged. This question has been extensively discussed in a previous article.[2]

As a result of the authors' work, it can be definitely stated that the cellobiose linking occurs to the extent of 24 per cent in each of the celluloses examined, and hence in this respect at least all the celluloses are similar. Since the acetolysis mixture is known to destroy appreciable amounts of cellobiose during acetolysis, 24 per cent is a minimal figure. Taking the unavoidable losses into consideration, the cellobiose linking may occur to the extent of nearly 50 per cent in each case.[9]

Furthermore, the rate of acetolysis in all celluloses examined is roughly the same. Whether or not the differences in cellobiose yields (24 to 35 per cent of the theoretical yield) are worthy of note is still an open question. The influence of small amounts of impurities on cellobiose yields has not been studied. However, the data show that there are appreciable variations in cellobiose yields in the case of the same purified cotton, if the experiments are made at different times even though similar technic is used.[10] This would indicate that very slight variations in the technic of acetolysis of cellulose or isolation of the cellobiose octa-acetate cause these differences and that the quantitative yield data in Table III, while very suggestive, cannot be interpreted too literally.

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[9] Freudenberg, *Ber.*, **44**, 767 (1921), who gives evidence regarding the percentage of cellobiose actually formed and lost during acetolysis, based upon experimental as well as theoretical grounds.

[10] Table III, Footnote *d*.

In the writers' opinion there are no data in the literature which would force the conclusion that the celluloses of the various seed-bearing plants are different chemical substances.

APPENDIX—OPTICAL PROPERTIES OF CELLOBIOSE OCTA-ACETATE

[By EDGAR T. WHERRY, Crystallographer, Bureau of Chemistry, Washington, D C]

Two samples of cellobiose octa-acetate prepared by Wise and Russell, one from cotton cellulose and the other from wood cellulose, were examined. They showed identical properties.

In ordinary light: Seen to consist of minute rods. Refractive indices (D):

$\alpha = 1.470$, $\beta = 1.480$, $\gamma = 1.505$, all ± 0.005; $\gamma - \alpha = 0.035$

Lengthwise of the rods index β is shown, while either of the others may be shown crosswise.

In parallel polarized light, Nicols crossed: Double refraction strong, the colors being bright gray, even on very thin crystals. Extinction parallel; elongation ±.

The technic used in identification is as follows: Use a microscope equipped with at least one Nicol prism, and ascertain the direction of the vibration plane of this Nicol. Immerse a small quantity of the substance in a drop of liquid with refractive index n near 1.48. Commercial liquid petrolatum is the most satisfactory, but almond oil, castor oil, or pseudo-cumene may also be used. Partially close the substage diaphragm, and center a broad crystal. Turn the stage until this crystal approaches parallelism with the cross hair indicating the vibration plane of the Nicol. If the substance is cellobiose octa-acetate, the crystal will disappear, and will remain invisible even on successively raising and lowering the microscope tube with the fine adjustment. This shows the refractive index lengthwise to be equal to that of the liquid, and this index is the most characteristic of the substance.

Immerse another sample in a liquid with n near 1.47, such as glycerol or turpentine, and observe the behavior of crystals on turning them into perpendicular position with reference to the vibration plane of the Nicol. Occasionally, a crystal will be found which will disappear in this position, showing its index crosswise to be equal to that of the liquid. Repeat with a liquid such as sandalwood oil or propyl iodide with n near 1.505. Under these conditions occasional crystals will also disappear, their index crosswise being the same as that of the liquid. In this way three refractive indices can be matched, and the identity of the substance as cellobiose octa-acetate may be definitely confirmed.

Effect of Hydrogen-Ion Concentration on Adsorption of Dyes by Wool and Mordants[1]

Preliminary Paper

By O. Reinmuth and Neil E. Gordon

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WORK in this laboratory on inorganic gels in connection with soil colloids led us to believe that the hydrogen-ion concentration played a very important role in (*a*) the adsorption of dyes, (*b*) the color which they imparted to the fiber, and (*c*) the manner in which they were adsorbed. The literature showed that very little had been done on the adsorption of dyes from solutions where special attention was paid to the hydrogen-ion concentration. Considerable work was carried out with this end in view, but its completion has been unavoidably delayed. In the meantime an article by Briggs and Bull[2] appeared practically covering the work which the authors had been carrying out on the color, adsorption, and hydrogen-ion concentration of fiber. However, Briggs and Bull did not take up any work on mordants, and the authors are therefore making a preliminary report on one of the mordants.

MATERIALS

Orange II was one of the dyes first used. Other dye baths are being used at the present. The wool was white sweater yarn of the best grade, washed, dried, and kept in a desiccator until used. The mordants used most were alumina and silica. When mordants were used without the wool they were prepared in the form of gels, as described in a previous article.[3] When the mordants were used with the wool, the gels were precipitated in the fiber.

EXPERIMENTAL

The baths were prepared of varying hydrogen-ion concentration by adding 0.1 N solution of sodium hydroxide or sulfuric acid. The ratio between the milligrams of dye and the weight of the wool or mordant was kept constant throughout the runs. The time allowed for equilibrium in each case was the same. The temperature of the bath was kept at the boiling point during adsorption. The amount of dye adsorbed by the pure wool, mordanted wool, or mordant alone was determined by titrating a sample of the dye solution before and after adsorption had taken place. Titanium chloride was used for determining the concentration of the dye, as suggested by Knecht.[4] The pH values of the bath were determined by the use of a hydrogen electrode.

The data obtained for the fiber were so much like those of Briggs and Bull that they will not be given in this preliminary report. The following table gives one an idea of results obtained when an acid, such as Orange II, is permitted to be adsorbed by a mordant, such as alumina, under a varying hydrogen-ion concentration.

EFFECT OF HYDROGEN-ION CONCENTRATION ON THE ADSORPTION OF DYES BY GELS

	Alumina Gel					
pH Value	Wet G.	Dry G.	Dye Used Mg.	Dye Adsorbed Mg.	Dye Left in Bath Mg.	Mg. Dye Adsorbed per G. of Gel
3.657	13.92	1.0231	525.0	283.9	241.1	278.2
3.753	14.13	1.0385	532.7	287.6	245.0	276.9
3.888	7.95	0.5843	299.7	120.2	179.6	205.9
4.145	11.17	0.8210	421.1	139.6	288.5	169.4
4.260	10.50	0.7417	395.8	117.4	278.4	152.2
4.514	9.43	0.6931	355.5	93.0	262.4	134.3
4.852	10.26	0.7541	386.8	82.9	303.9	111.0
5.021	13.65	1.0023	514.5	45.0	469.5	44.9
5.393	14.33	1.0532	540.2	47.1	493.1	42.2

This marked change of adsorption with the small change in pH value makes it quite evident that a control of hydrogen-ion concentration is a most important factor in the dye industry. There is also a marked change of color with a change of hydrogen-ion concentration. This was especially noticeable with some dyes and at certain pH values. A full discussion of this and change of color with the strong adsorption of dye will be reported in a later paper.

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[1] Presented before the Division of Dye Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *J. Phys. Chem*, **26**, 845 (1922).

[3] *Soil Sci.*, **15**, 157 (1923).

[4] *Ber.*, **36**, 1552 (1903); **40**, 3819 (1907).

The Chemical Properties of Cotton Linters[1,2]

By William F. Henderson

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By treating cotton linters with strong acids it was found that the copper numbers were increased considerably as long as the acid concentrations were low, but very rapidly when the acid concentrations were high. With weak acids the change in copper numbers was slight for all concentrations. When the linters were treated with alkalies, the copper numbers remained practically constant.

Various methods for preparing viscose from linters were tried. Preliminary acid treatment of the linters produced a marked effect upon the viscosity of the viscose solutions. The effect upon the viscosity was much more pronounced than that on the copper numbers.

THE purpose of this investigation was to obtain more definite information concerning the chemical reactions of cotton linters. Although the quantity of linters produced is subject to wide variation, the amount of this material which is available is large. The peak of the annual production was reached in 1916, when over a million and a quarter of the 500-lb. bales were produced. That the supply is fairly large and the cost of production low has been recognized to some extent, and large quantities of linters are used in the paper and nitrocellulose industries. Other industries use linters in considerable quantities, and doubtless there will be many additional opportunities for application. It has been the author's aim to discover some of the properties of linters which will make possible further applications of this type of material.

PHYSICAL CHARACTERISTICS

Under the microscope linters show the same characteristics as ordinary cotton fibers. They are colorless, transparent, and present a flattened, ribbon-like appearance. The fibers are hollow, the lumen showing up very plainly in unstained preparations. A characteristic twisting is revealed, just as in the case of long cotton fibers. The linters differ from long-fiber cotton apparently only in length.

The linters used for this research were almost pure white in color, but when compared with a sheet of white paper a faint yellow tint could be detected, due to the presence of a small amount of iron salts on the fiber. When immersed for a few minutes in strong hydrochloric acid, this iron dissolved out, imparted a yellow color to the acid, and ammonium thiocyanate showed the presence of iron in the acid solution. When washed free from this acid solution, pure white fibers remained.

ANALYTICAL CHARACTERISTICS

MOISTURE—Linters are hygroscopic, and when dried in air will retain from 5 to 6 per cent of their own weight of water. Determinations of the moisture content were made by noting the loss in weight when the air-dried samples were heated for 2 hours at 110° C. and the material cooled in a desiccator. The following data are typical for the type of linters used:

MOISTURE	Per cent
Air-dried	5.56
Saturated air	14.89

For ordinary cotton fiber the water content usually ranges from 6 to 8 per cent. In a saturated atmosphere, Wiesner[3] found a water content of 20.99 per cent for cotton cellulose.

EXTRACTION WITH SOLVENTS—Extractions were made on linters, using for solvents, water, chloroform, and ethyl alcohol. A Soxhlet apparatus was employed and the solvent afterwards was distilled and the residue weighed.

Samples dried at 105° to 110° C. were used in each case. The results of the extractions were as follows:

SOLVENT	Per cent Extract
Water	0.310
Chloroform	0.415
Ethyl alcohol	0.575

ASH—The material showed a low percentage of ash, the average of several determinations giving 0.230 per cent. Bleached cotton, according to Schwalbe,[4] should give on the average about 0.5 per cent of ash, although Cross and Bevan[5] found the ash content to range from 0.1 to 0.4 per cent.

COPPER NUMBER—The copper number, or copper index, is a value based on the reduction of copper in Fehling's solution. The standards of comparison are purely arbitrary, and consistent results depend entirely upon well-controlled, uniform conditions for all the determinations to be made. The method used by the author was very similar to that recommended by Schwalbe.[6]

An oven-dried sample, weighing from 1 to 2 grams, was covered with 250 cc. of water and the mixture brought to boiling. Fifty cubic centimeters of each part of Fehling's solution were boiled, the two parts mixed, and the mixture added to the water containing the cellulose. The whole was boiled exactly 15 minutes, with stirring, in an all-glass reflux apparatus. After filtration through a Buchner funnel (diatomaceous earth was unnecessary), the linters were washed with hot water until the filtrate showed no copper when tested with ferrocyanide. The linters were treated with 7 per cent nitric acid, warmed, and filtered. After rinsing they were treated with dilute ammonia water, warmed, filtered, and then treated again with dilute nitric acid, and finally washed free from copper. The filtrates and washings were concentrated and the copper determined by titration with thiosulfate.

The copper determined by this method represents the "total copper," which consists of that which is precipitated as cuprous oxide during the reduction, and also the trace of unreduced copper which cannot be removed from the fibers by washing with hot water. In order to determine the amount of copper reduced, this small amount of unreduced copper which adheres so tenaciously to the linters must be determined and the amount subtracted from the total copper. The unreduced copper was determined by treating the linters with cold Fehling's solution. The removal and determination of the copper were accomplished in the manner described above. This copper has been termed "correction" in the data concerning copper numbers in this paper.

The linters used in this research gave the following results for copper number determinations, calculated on the basis of 100 grams of oven-dried material:

	Per cent
Total copper	1.03
Correction	0.46
Reduced copper (difference)	0.57

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[1] Presented before the Division of Cellulose Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Abstract of a thesis submitted to the University of Pittsburgh in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] Wiesner, "Die Rohstoffe des Pfanzenreiche," 2nd ed., **2**, pp. 181 and 250; Matthews, "Textile Fibers," 3rd ed., p. 174.

[4] "Chemie der Cellulose," p. 34.

[5] "Cellulose," 2nd ed., p. 3.

[6] "Chemie der Cellulose," p. 625.

Summary of Properties—A resumé of the preliminary treatment given the linters during the course of manufacture, with the analytical figures determined, points very clearly to the fact that these linters are cellulosic material of exceptional purity.

Preliminary Treatment:

(1) Dirt dusted out
(2) Boiled 5 hours in 1 per cent NaOH
(3) Bleached with very weak hypochlorite
(4) Dried at low temperature

Analytical Constants:

(1) Moisture, 5.5 per cent
(2) Extracted material, 0.31 to 0.57 per cent
(3) Ash, 0.13 per cent
(4) Copper reduction, 0.57 per cent

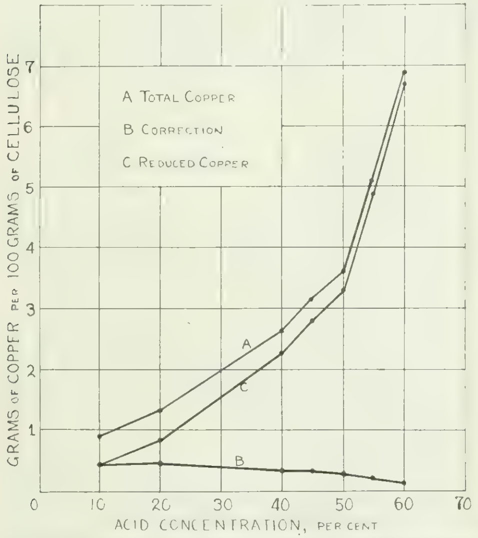

Fig 1 Copper Numbers of Cotton Linters Treated with H_2SO_4 for 16 Hours at 25° C.

Action of Certain Halogen Compounds on Linters

Phosphorus Oxychloride—Phosphorus oxychloride reacts with linters in the cold, and after several hours shows a marked tendency to disintegrate the fibers. The action is very similar to that produced by hydrochloric acid, which is discussed below.

Selenium Oxychloride—Cold selenium oxychloride produced no visible change in oven-dried linters after 24 hours. When warmed to approximately 75° C. the linters softened, disintegrated, and finally the mixture became a deep brown liquid. A small amount of hydrogen chloride was evolved during the process. One hundred and fifty cubic centimeters of anhydrous ethyl ether were added to the cooled solution and a pale cream-colored, amorphous precipitate settled out. This substance quickly decomposed in the presence of a trace of moisture, turning bright red (selenium) and evolving hydrogen selenide.

Action of Acids on Linters

Linters were treated with different acids of varying concentrations for several hours, and, after washing and drying, the copper numbers were determined. The acids used were sulfuric, hydrochloric, hydrobromic, nitric, phosphoric, formic, and acetic. The concentrations ranged from 10 to 100 per cent, depending upon the acid. The time of exposure in most cases was 18 hours. The temperature was 25° C. in all cases. The results are given in the accompanying table and in Fig. 1. The results for sulfuric acid are plotted as representative of the action of strong acids on linters.

Effects of Acids on Copper Numbers of Linters

Aqueous Sulfuric Acid, 16 Hrs. (Fig. 1)

Per cent Acid	Total Copper Per cent	Correction Per cent	Copper Number
10	0.88	0.44	0.44
20	1.33	0.49	0.84
40	2.64	0.34	2.30
45	3.16	0.34	2.82
50	3.59	0.29	3.30
55	5.10	0.20	4.90
60	6.88	0.14	6.74
Aqueous Hydrochloric Acid, 20 Hrs.*			
10	2.01	0.47	1.54
15	2.48	0.42	2.06
20	3.86	0.40	3.46
25	5.66	0.34	5.32
30	6.94	0.31	6.63
34	7.35	0.25	7.10
Aqueous Hydrobromic Acid, 18 Hrs.			
10	1.75	0.56	1.19
20	1.88	0.39	1.49
30	3.46	0.35	3.11
34	4.17	0.37	3.80
Aqueous Nitric Acid, 18 Hrs.			
10	1.00	0.46	0.54
20	1.32	0.41	0.91
30	1.61	0.42	1.19
40	2.10	0.40	1.70
50	3.51	0.39	3.12
60	10.53	0.44	10.09
70	26.99	1.21	25.78
Aqueous Phosphoric Acid, 18 Hrs.			
10	1.00	0.48	0.52
30	1.08	0.45	0.63
60	1.47	0.42	1.05
70	1.69	0.43	1.26
80	1.98	0.46	1.52
Aqueous Formic Acid, 18 Hrs.			
10	0.83	0.43	0.40
20	0.88	0.41	0.47
40	0.95	0.39	0.56
60	1.22	0.39	0.83
78	1.16	0.30	0.86
Aqueous Acetic Acid, 18 Hrs.			
20	0.59	0.34	0.25
40	0.60	0.33	0.27
60	0.75	0.40	0.35
80	0.98	0.43	0.55
100	1.14	0.46	0.68

* When linters were treated for 18 hours with anhydrous ethyl ether, saturated with dry hydrochloric acid gas, a reaction somewhat similar to that in aqueous solution was noted. The linters in this case gave copper values as follows:

	Per cent
Total copper	I, 3.29; II, 3.17
Average	3.23
Correction	0.59
Copper number	2.64

Action of Alkalies on Linters

Experiments were conducted using alkalies with linters in a manner similar to that employed for acids. The alkalies used were sodium, potassium, and ammonium hydroxides. The following tables and Fig. 2 show the results of these experiments:

Aqueous Sodium Hydroxide, 18 Hrs., 25° C.

Per cent Alkali	Total Copper Per cent	Correction Per cent	Copper Number
10	1.10	0.57	0.53
15	1.81	1.12	0.69
20	2.06	1.37	0.69
30	2.03	1.34	0.69
50	2.14	1.36	0.78

These results agree with the idea presented by Hibbert,[7] that alkalies do not open up one of the cellulose rings. The constancy of the copper reduction values bears out this observation.

Aqueous Potassium Hydroxide, 18 Hrs., 25° C.

Per cent Alkali	Total Copper Per cent	Correction Per cent	Copper Number
10	1.04	0.50	0.54
15	1.07	0.61	0.46
20	1.32	0.77	0.55
30	1.89	1.18	0.71
50	2.04	1.39	0.65

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[7] This Journal, **13**, 256, 334 (1921).

Ammonium Hydroxide. Concentrated ammonium hydroxide, containing 28.3 per cent of ammonia, was tried with linters. The copper values were almost the same as were found for untreated cellulose, being as follows:

	Linters + NH_3	Original Linters
Total copper	1.10	1.03
Correction	0.49	0.46
Copper reduced	0.61	0.57

It is evident that concentrated ammonium hydroxide at 25° C. has no appreciable effect upon the linters.

Ester Formation with Linters

In the past twenty years an immense amount of work has been done with the esterification of cellulose. The formation of nitrates, acetates, benzoates, formates, lactates, etc., has been carefully studied, and almost innumerable patents have appeared covering the various methods of production.[8] The author has not endeavored to add to this long list of methods, but has attempted the application of a few of the well-tried processes to the preparation of esters from linters. During the war the formation of cellulose nitrates from linters was investigated thoroughly and carried out on an immense scale by the War Department. The author devoted his attention to the production of the benzoate, and especially to the production of the dithiocarbonate, commonly known as viscose.

Benzoate—The method most commonly used for the formation of cellulose benzoate is one which proceeds according to the Shötten-Baumann reaction. The application of this method to cellulose was investigated by Ost and Klein.[9] This method involved the use of benzoyl chloride with cellulose in the presence of a base. The most successful preparation of the tribenzoate of cellulose resulted when pyridine was used as the base. The discussion of this reaction is given by Heuser.[10]

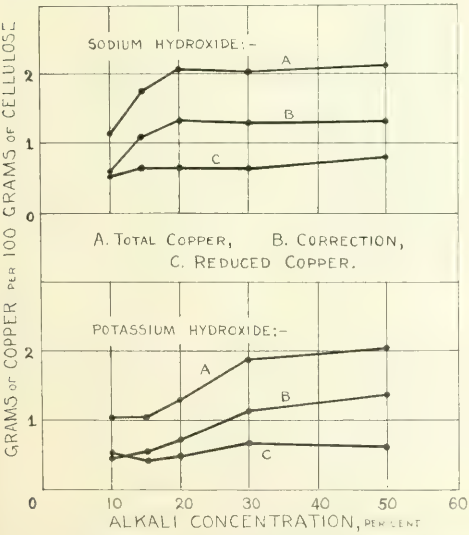

Fig 2—Copper Numbers of Cotton Linters Treated with Alkalies for 18 Hours at 25° C.

When this method was tried by the author, with linters, it was found that the esterification occurred very readily. The tribenzoate was produced and it was completely soluble in chloroform, producing a very viscous solution.

Dithiocarbonate—Most of the author's research in regard to esters has been in connection with cellulose dithiocarbonate, or viscose, as it is usually called. This ester was discovered by Cross and Bevan, who patented their discovery in 1893.[11] A description of the preparation of viscose and its properties has been given by these chemists in their book, "Cellulose," and it has now become one of the important subjects in every general treatise on cellulose chemistry.

The successful production of viscose depends upon the many factors which may be classified in a general way as follows:

(1) Preliminary treatment of the cellulose
(2) Concentration of reagents employed
(3) Temperature control
(4) Time allowed for stages of the reaction

In general, the program carried out may be divided into three stages:

(1) Formation of alkali cellulose
(2) Combination of alkali cellulose with carbon disulfide
(3) Solution of the ester in water

The formation of the alkali cellulose is accomplished by the interaction of cellulose and sodium hydroxide solution. Not only is the combination of cellulose with alkali to form alkali cellulose necessary, but a process of "ripening" is also important. This process consists merely in allowing the alkali cellulose to stand several hours before attempting to apply the carbon disulfide. In a patent[12] granted to the discoverers of viscose, claim was made that the alkali and carbon disulfide could be applied simultaneously, but in the manufacture of viscose at the present time the alkali cellulose is allowed to ripen before the carbon disulfide is applied. The ripening may be carried out in a closed vessel or it may be accomplished by exposing the alkali cellulose to the air. The temperature at which the ripening occurs has an important bearing on the quality of viscose produced. Carbon disulfide is added and the mixture sealed up to prevent loss of carbon disulfide vapor. The carbon disulfide vapor reacts with the alkali cellulose, and the whole mass becomes yellow and finally orange in color. If the reaction proceeds properly, the fibers eventually melt together into moist, gelatinous masses. Here also the temperature affects the speed of the reaction. At 4° C. at least 48 hours are necessary, while at 25° C. usually 18 hours are sufficient.

When the combination of alkali cellulose with carbon disulfide is complete, any excess of carbon disulfide is removed by suction, and water and usually more sodium hydroxide are added to the cellulose ester. The dissolving of the ester is usually slow, due to the great viscosity of the solution. Frequent agitation is desirable. As the solution process is carried out the material is stored in a refrigerator, where it must be henceforth kept to prevent rapid decomposition. The quality of the various solutions is subject to wide variations unless great care has been exercised to control the conditions under which these solutions have been prepared.

Freshly prepared viscose must be subjected to another ripening process if the product is to be used for producing threads or films. Cellulose dithiocarbonate is not a very stable substance and will decompose at room temperature in the course of 2 or 3 days. This decomposition occurs very slowly at 4° C.; consequently, the preparations must be preserved in a refrigerator. The ripening consists in allowing this decomposition to proceed to the point where the properties of the product are most suitable for the application in mind.

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[8] Worden, "Technology of Cellulose Esters," Vol. 1, p. 3088.

[9] *Z. angew. Chem.*, **26**, 437 (1913).

[10] "Lehrbuch der Cellulose Chemie," p. 56.

[11] Brit. Patent 5700 (1893).

[12] U. S. Patent 520,770.

A great many modifications of the methods described in general in the literature have been tried by the author of this paper, in the effort to discover the best conditions under which viscose could be produced from linters. It is generally recognized by workers in this field that viscose made from wood pulp is more readily dissolved in water than that made from very pure forms of cellulose, such as cotton. It is also generally known that viscose made from wood pulp produces films, or threads, which are not as strong as those produced from the purer forms of cellulose.

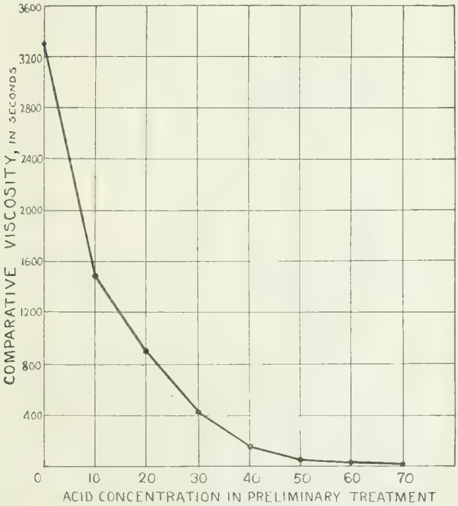

Fig. 3 Comparative Viscosity of Solutions of Viscose Made from Cotton Linters Treated with Nitric Acid

Experiments were conducted in which the conditions of formation of the alkali were tried, and both temperature and time of exposure were varied. The conditions under which the alkali cellulose was ripened were varied and the effects noted. In many of these preparations the alkali reaction was not complete and the resulting xanthogenate would not dissolve in water. In others the alkali reaction had gone too far and, while complete solubility of the ester often resulted, the viscosity of the solution was very low. A method suggested by Mitscherling[13] for the production of viscose from cotton was tried out with linters. This method was briefly as follows:

One hundred grams of linters were treated with 750 grams of 20 per cent sodium hydroxide for 20 minutes at 25° C. Alkali was pressed out under pressure and the pressed alkali cellulose weighed 360 grams. This was exposed to air for 44 hours at 25° C. It was then placed in a bottle, 50 grams of carbon disulfide added, and the bottle sealed. The mixture was allowed to stand at 25° C. for 18 hours.[14] Fifty grams of sodium hydroxide were dissolved in a liter of water and this solution was added to the xanthogenate. The whole was made up to 2000 grams. The solution was practically complete, but the product was thin and watery, and very unsatisfactory for most applications.

This very low viscosity of the product just described reminded the author of a series of viscose preparations which he had made earlier from partially hydrolyzed linters. These preparations were likewise low in viscosity. In a series of experiments in which the method suggested by Mitscherling's paper was modified, it was found that by shortening the time of exposure of the alkali cellulose to air (ripening) the viscosity of the product became much greater. When the time was shortened to 5 hours, a product of high viscosity and other fine qualities was produced.

Reference was made earlier in this discussion to the effect on viscose of preliminary treatment of the cellulose. Herein apparently lies the reason for the difference in properties of wood-pulp viscose and cotton viscose. The treatment through which wood pulp goes in order to free the cellulose from lignin, etc., is more drastic than that through which cotton is put. The effect is noticed in the more rapid solution of viscose made from wood pulp than that made from cotton, and at the same time the production of weaker threads or films by the former when compared with those from the latter.

This was borne out by a series of experiments performed by the author. Samples of linters were treated for varying lengths of time with hydrochloric acid and afterwards washed until neutral. Viscose was made from these acid-treated linters, and in every case very thin watery products were formed. The cellulose was rendered much more reactive by the acid treatment, but the products made from the viscose possessed very little strength.

The final piece of work in connection with this research consisted in the preparation of viscose from samples of linters which had been treated with increasing concentrations of nitric acid.

Thirty-gram samples of linters were treated with nitric acid solutions ranging from 10 to 70 per cent, for 18 hours at 25° C. After washing thoroughly, until free from acid, these samples were dried at room temperature. Each sample was converted into viscose, using identical conditions for all. A blank (untreated fibers) was run for a comparative test. The blank test gave viscose which possessed the highest viscosity of all the samples, and in the acid-treated samples the viscosity fell with great rapidity. A Störmer viscometer was used to gain some idea of the comparative viscosities. The results of these tests were as follows:

Per cent Acid Used for Preliminary Treatment	Number of Seconds for 100 Revolutions
0	3300
10	1500
20	900
30	420
40	178
50	50
60	27
70	7
Water	5

The greatest diminution of viscosity occurred when the lowest concentration of acid was used. This is readily seen when the figures are plotted, as in Fig. 3.

Acknowledgment

The author wishes to express his appreciation to W. A. Hamor, of Mellon Institute, and to Alexander Lowy, of the University of Pittsburgh, for many helpful suggestions during the course of this research.

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[13] Paper presented before the Section of Cellulose Chemistry at the 62nd Meeting of the American Chemical Society, New York, N. Y., September 6 to 10, 1921.

[14] Mitscherling proposed the use at this point of sodium hydroxide *equal* to the weight of the original cellulose.

Zanetti Appointed on Committee of League of Nations

J. Enrique Zanetti has been appointed to a committee of the League of Nations which will investigate the whole question of chemical warfare. Associated with Dr. Zanetti, who is now in England on leave of absence from Columbia during the next academic year, will be a group of chemists representing other countries, among whom will be Sir William Jackson Pope, of Cambridge University, England, and Charles Moureu, of the University of Paris.

Furfural from Corncobs[1]

II—The Bureau of Chemistry Experimental Plant and Process for Furfural Production

By **Frederick B. LaForge** and **Gerald H. Mains**

Bureau of Chemistry, Washington, D. C.

In this paper the work of the Bureau of Chemistry in the production of furfural from corncobs, and the experimental plant and process developed in the course of the work are described. The plant consists essentially of a pressure digester unit and a continuous column still. The cobs are digested with water and high-pressure steam, the vapors being condensed to form a dilute furfural solution which is concentrated in the column still.

Optimum operating conditions are: Pressure, 130 to 135 pounds (180° C.); ratio of water to cobs, 4:1; digestion period, 2 hours. The furfural yield obtained is 6 per cent of the weight of cobs used. The column still separates from the dilute solution 5 to 6 pounds of crude (95 per cent) furfural per hour with a 97 to 98 per cent recovery. Small quantities of acetic acid, acetaldehyde, and methanol are by-products.

The process is simple and commercially feasible, and can be adapted to a number of agricultural wastes.

WORK in the Bureau of Chemistry on the utilization of corncobs started in 1918, resulted in the development of processes for the manufacture of various products,[2] including corncob adhesive.[3] In 1920 Monroe, of this bureau, obtained furfural by the action of fairly concentrated sulfuric acid upon this adhesive.[4] The possibility of thus producing furfural cheaply led to a study of possible uses of the material as an organic intermediate. As the minimum price quotation from chemical supply houses was $30 per pound, it was decided to produce the furfural for experimental work in the bureau.

About 60 pounds of furfural were produced during the winter of 1920–21, using a small Duriron digester adopted as the result of laboratory experiments on sulfuric acid digestion of the adhesive and of the cobs themselves. Interest in the possibilities of furfural utilization had been aroused among commercial firms, and a considerable portion of the material made was supplied to these manufacturers for coöperative research. Preliminary results of this coöperation were so promising that a study of furfural production on a semicommercial scale was undertaken. The previous experimental work had shown that the procuring of a maximum yield of furfural was not the determining factor of low cost, but that the main consideration should be given to the time, labor, heat, and digestive agents required. The sulfuric acid digestion gave good yields, but was deficient in the other points.

Several investigators had noted the formation of furfural by the action of steam or superheated water on various vegetable materials.[5] Furfural had been isolated from the vapors accompanying the production of corncob adhesive, and experiments[6] showed the possibility of obtaining promising yields from the cobs by steam digestion under pressure.

A steel digester designed for the production of adhesive was accordingly put into use, and large quantities of dilute furfural solutions were produced. A study of the system furfural–water[7] made it possible to work out conditions for the ready concentration of the furfural by fractional distillation, and small temporary stills were used until a suitable column could be designed. Several manufacturers of distillation equipment coöperated with the bureau in the design of apparatus for concentrating the dilute furfural solutions, using data obtained in the experimental work. Specifications were drawn up for a continuous column still utilizing the various designs suggested, and the column was put into operation in January, 1922.

During 1921, using the digester and temporary rectifying stills, more than 220 pounds of furfural were made at the experimental plant, this quantity of material being required for the developing coöperative work on furfural utilization. The erection of the column still gave the plant a maximum capacity of 40 to 50 pounds of furfural per working day. The latter part of January, 1922, commercial furfural was offered on the market in this country at a comparatively low price through the independent research of the Miner Laboratories of Chicago. The increasing demand for furfural by the more important coöperators was taken care of by this development, thus permitting attention to be turned from quantity production to experimental work. During the experimental runs in 1922 approximately 350 pounds of furfural were produced, 95 pounds during a single 21-hour continuous run.

The Plant

The furfural plant occupies a portion of the main floor space of the building of the Color Laboratory at Arlington Farm, Rosslyn, Va. This building is a factory type structure, provided with all necessary facilities for large-scale experimental work, including high and low-pressure steam and electrical power. A traveling crane serves for the lifting and transporting of materials and for the erection of heavy apparatus. The equipment consists of two parts—a digester unit for the production of dilute furfural solution, and a column still for the separation of furfural from this solution.

Digester Unit—The digester proper is a cylindrical steel shell, 72 inches high by 36 inches in diameter, with a conical bottom. It has an available capacity of about 30 cubic feet and holds a charge of 200 to 250 pounds of cobs, with the necessary amount of water. The digester and accessories are shown in Figs. 1 and 2, and diagrammatically in Fig. 3. There is a 15-inch charging door at the top of the digester and a 12-inch standard garbage-reducer type gate valve at the bottom. The digester is provided with a steam gage, thermometer well, and safety valve. The steam, controlled by a pressure regulator, enters near the gate valve. The blow-off vapors pass to the condenser through an exit pipe near the top of the shell, the opening being placed as high as possible to minimize the entrainment of solid and liquid particles.

Beneath this digester is a wooden box connected with the bottom opening of the gate valve. This box has an inclined slatted bottom, covered with a screen, which serves to drain the discharged contents of the digester. The liquids are caught in a shallow wooden tank under the drain box. A hydraulic press to handle the wet residue is placed conveniently near the drainage tank.

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[1] Received May 12, 1923.

[2] LaForge, This Journal, **10**, 925 (1918).

[3] LaForge, *Chem. Age* (*N. Y.*), **28**, 332 (1920).

[4] U. S. Patent 1,357,467 (November 2, 1920); This Journal, **13**, 133 (1921).

[5] Williams, *Chem. News*, **26**, 231, 293 (1872); Müller, *Ibid.*, **26**, 247 (1872); Hill, *Am. Chem. J.*, **3**, 33 (1881); Heuser, *Z. angew. Chem.*, **27**, 654 (1914).

[6] LaForge, This Journal, **13**, 1024 (1921).

[7] Mains, *Chem. Met. Eng.*, **26**, 779 (1922); **26**, 841 (1922).

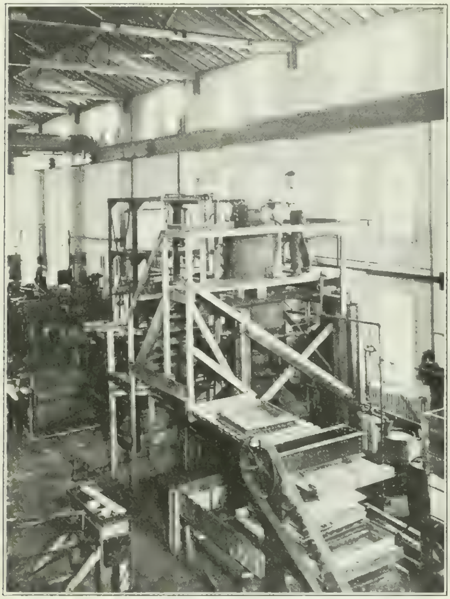

FIG. 1—FURFURAL PLANT, SHOWING DIGESTER AND PRESS

The condenser for the furfural-laden blow-off vapors is of the vertical copper tube type. The condensed vapors are collected in barrels or in a small receiver, from which the liquid is pumped to a storage tank.

COLUMN STILL—The continuous column still (Fig. 2) used in the experimental plant consists of a column with exhausting and rectifying sections, a condenser for the minimum boiling furfural-water distillate, a condenser for the heads, a decanter, feed and receiving tanks, and accessories.

Fig. 4 is a diagrammatic representation of the still. The exhausting and rectifying sections of the column are built of standard 8-inch plate units. There are 12 plate and boiling cap units, 6 inches high, in the exhausting section and 21 perforated plate units, 4 inches high, in the rectifying section. A 24-inch dephlegmator section at the top and a 12-inch bottom section containing the open steam sprayhead complete the column proper. The condensers consist of copper coils enclosed in galvanized iron tanks. The decanter and receiving tanks are of copper, the receiving tanks being tin lined. The feed tank is of galvanized iron and has a capacity of 100 gallons. All piping except for condensing water is of copper.

The dilute furfural solution from the digester is pumped from its storage tank to the feed tank, whence it flows by gravity onto Plate 12 at the top of the exhausting section, *A*. Distillation is effected by means of open steam entering the bottom of the column through the pressure regulator, *R*. In the exhausting section the furfural is vaporized and carried, together with water and the more volatile components, into the rectifying column, *B*, which separates from this vapor a minimum boiling mixture of furfural and water containing approximately 35 per cent of furfural and boiling at 97.9° C. This furfural-water mixture is drawn off through the main vapor pipe, *C*, and passes through the condenser, *D*, into the decanter, *E*. Since at room temperature furfural is soluble in water to the extent of only about 8 per cent, the excess furfural separates as a lower layer, while the upper saturated solution of furfural in water flows off through the return pipe *F*, as reflux to the column, entering it at Plate 14. The lower furfural layer, which contains approximately 5 per cent of water, is drawn from the bottom of the decanter continuously, and passes through the tester, *G*, to the receiving tank, *H*. This furfural, containing a small quantity of other impurities besides the water, is known as crude or technical furfural, and as such is ready for use in the trade.

The feed liquor contains a small quantity of lower boiling impurities, which are carried through to the upper part of the rectifying column and pass off as heads through the vapor pipe, *K*, and condenser, *L*, to the receiving tank, *M*. The dephlegmator, *J*, helps to provide reflux for the upper portions of the rectifying column.

The organic acid contained in the feed liquor passes toward the bottom of the exhausting column, and is carried off with the water by the discharge pipe, *S*, to the sewer. The vent, *V*, open to the air, takes care of any sudden change of pressure in the lower part of the column.

Regulating accessories include four valve-controlled branches of the main vapor pipe leading from different plates of the rectifying section, drain cocks from each plate, pressure gage, the thermometer, T_1, at the feed plate, and the thermometers, T_2 and T_3, inserted in the vapor pipes.

STEAM DIGESTION PROCESS

The optimum conditions as determined by the laboratory experiments[8] gave a furfural yield of about 9 per cent (based on air-dry weight of cobs) starting with a water to cob ratio of 6 : 1 and distilling off about 60 per cent of the water during the reaction period of 2 hours with temperature of 180° C.

In the experimental plant, since the digester is heated by the injection of steam, the water to cob ratio at any stage of the process necessarily differs from that existing in the externally heated laboratory autoclave. Runs were made using various proportions of water to cobs to adjust properly the conditions. The best results were obtained where a ratio of 4:1 was reached after 30 minutes at 130 to 135 pounds gage pressure (180° C.).

In order to obtain the 900 pounds of water (at the end of 30 minutes digestion) for the usual charge of 200 to 225 pounds of cobs, it was necessary to start with about 550 pounds of water at room temperature, condensation making up the difference.

In experiments on this scale, no difference in results was observed in the use of whole or broken cobs. In fact, the material is practically all disintegrated during the early stages of the digestion.

PROCEDURE—About 550 pounds of water, or weak furfural solution, and from 200 to 225 pounds of cobs are placed in the digester, and steam at 150 pounds boiler pressure is slowly run in. The time when the pressure in the digester has reached 130 pounds is recorded as the beginning of the reaction period. At this point the blow-off valve is opened slightly and the rate of distillation regulated to 1 to 1.5 pounds per minute. This allows the escape of gases as they are formed. After 30 minutes the blow-off rate is increased to 5 to 6 pounds per minute and the digestion continued for 90 minutes longer. At that point the steam is shut off[9]

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[8] LaForge, THIS JOURNAL, **15**, 499 (1923).

[9] In some cases, when the pressure has fallen to 10 or 12 pounds, a slow current of steam is admitted into the digester in order to expel a larger proportion of the furfural dissolved in the liquid. It is doubtful, however, whether this is necessary or advisable if the rate of distillation during the process is properly regulated.

TABLE I—PRODUCTION OF FURFURAL USING WATER-COB RATIO LESS THAN THE OPTIMUM

Run	Weight of Charge: Cobs Lbs.	Weight of Charge: Water Lbs.	Time for Heating to 180° C. Min.	Time of Digestion Min.	Time of Main Blow off (Pressure, 135–12 Lbs.) Min.	Time of Blow-off at 12 Lbs. Min.	Weight of Total Distillate Lbs.	Furfural in Distillate: Concentration Per cent	Furfural in Distillate: Weight Lbs.	Discharge Liquor Lbs.	Furfural in Discharge Liquor Lbs.	Total Furfural Produced Lbs.	Yield[a] Per cent
A 1	240	372	13	140	20	20	381	3.22	12.3	893	3.0	15.3	6.38
A 2	240	385	10	132	20	30	361	3.27	11.8	870	3.1	14.9	6.21
A 3	255	444	23	115	15	75	613	2.35	14.4	900	1.5	15.9	6.24
A 4	226	390	12	127	23	15	510	2.31	11.8	852	2.2	14.0	6.20

[a] Based on air-dry weight of cobs.

TABLE II—FURFURAL PRODUCTION USING WEAK FURFURAL SOLUTION IN CHARGE[a]

Run	Weight of Charge: Cobs Lbs.	Weight of Charge: Weak Furfural Solution Lbs.	Furfural Added with Charge Lbs.	Time for Heating to 180° C. Min.	Time of Digestion Min.	Time of Main Blow-off (Pressure, 135–12 Lbs.) Min.	Time of Blow-off at 12 Lbs. Min.	Weight of Total Distillate Lbs.	Furfural in Distillate: Concentration Per cent	Furfural in Distillate: Weight Lbs.	Discharge Liquor Lbs.	Furfural in Discharge Liquor Lbs.	Total Furfural Minus Added Furfural Lbs.	Yield[b] Per cent
B-1	245	390	4.8	10	120	25	30	541	3.05	16.5	828	3.6	15.3	6.25
B-2	245	390	1.8	15	127	23	15	447	3.32	14.8	843	2.8	15.8	6.45
B-3	228	390	4.0	8	127	18	0	564	2.91	16.4	737	1.7	14.1	6.18

[a] Water–cob ratio, like that in Table I, is (after 30 minutes digestion) about 3:1 whereas the optimum is 4:1.
[b] Based on air-dry weight of cobs

and the blow-off increased from time to time as the pressure falls.

The distillate collected throughout the run contains the major portion of the furfural formed in the process. The composition varies at different stages of the digestion. Furfural begins to appear in the distillate about 15 minutes after the temperature reaches 180° C. The concentration increases for 60 minutes, remains nearly constant for 30 minutes, and then decreases rapidly. Therefore, the entire distillate from one or more runs is mixed together to get a uniform solution suitable for subsequent concentration in the column still.

When the pressure of the digester has dropped to about 5 pounds the contents are discharged, allowed to drain for 15 to 20 minutes, then pressed to expel additional liquid. The small quantity of dissolved free furfural is recovered from the extract by distilling off about one-third of its volume. The dilute furfural thus obtained is added to subsequent charges of cobs. The added furfural, together with that formed from the cobs, distils off, thus increasing the concentration of the distillate and making possible a recovery of practically all the available furfural. The cellulosic press cake and the residual extract liquor from which the furfural has been recovered are usually discarded.

DATA FROM TYPICAL RUNS—Table I gives data from a series of runs made in the earlier stages of the work before the optimum water–cob ratio had been determined. The charge of water used would give a water–cob ratio at the end of 20 minutes digestion nearer 3:1 than the optimum 4:1. The slight variations occurring in this ratio and in the time relations were not sufficient to affect the yield materially.

The column headings are for the most part self-explanatory. The quantities of furfural were determined in the distillate by the usual phloroglucin method. The free furfural in the discharge liquor was determined by distilling off 80 cc. from 100 cc. and determining the furfural in an aliquot part of the distillate. The column headed "Yield" gives results based on analysis of the solutions. The phloroglucin precipitates contain a small amount of impurities, and a number of experiments on actual isolation show that the true furfural value will average 95 per cent of the calculated value. The wet cellulosic residue was weighed and the moisture was determined in an aliquot part. The weight of moisture in the residue added to the weight of the liquor obtained by draining and pressing gives the weight of discharge liquor.

In Run A-3 an attempt was made to increase the rate of distillation in order to reduce to a minimum the furfural content in the liquid remaining in the digester. Under the conditions employed, it was, indeed, possible to expel about half of the quantity which would otherwise have remained in the discharge liquor. This advantage, however, is more than offset by the lowered concentration of the distillate, the added steam consumption, and the increased time of operation.

In the second series of runs (Table II) a weak solution of furfural instead of water was used in the charge. Its furfural content in each case was determined by analysis, and in calculating the yield for the run the quantity of furfural added with the charge was subtracted from the total furfural obtained. The data from these runs show that practically all the furfural added with the charge, together with that produced during the run, can be recovered, making possible a convenient recovery of furfural from any very dilute solutions formed in the process.

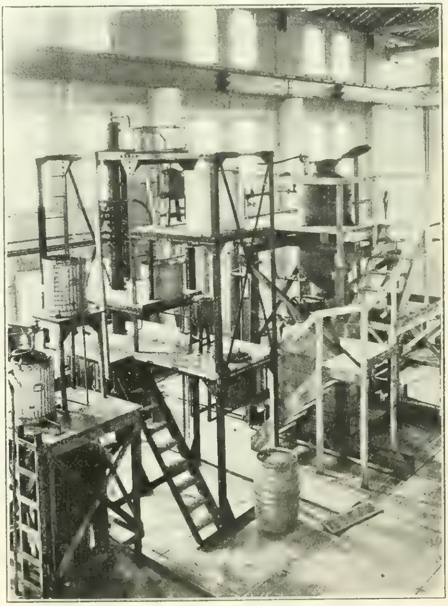
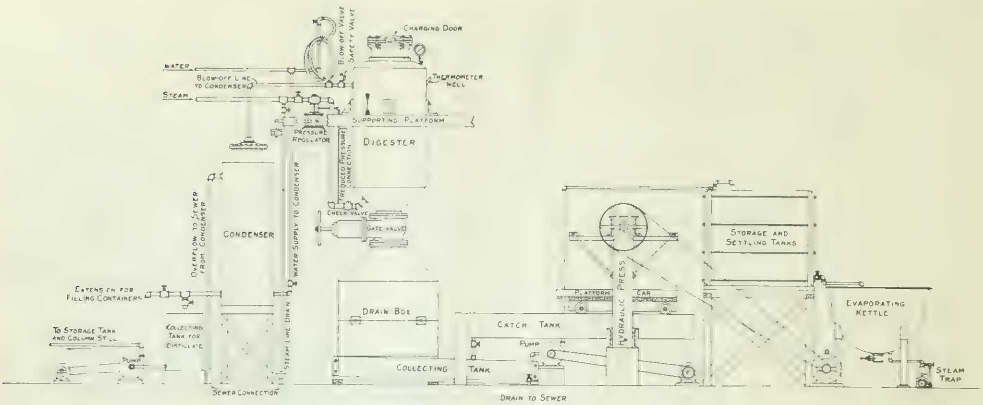


FIG. 2—FURFURAL PLANT, SHOWING COLUMN STILL AND DIGESTER

At this stage of the investigations small-scale laboratory experiments showed that the optimum water–cob ratio was about 4:1. With a digester charge of 500 to 600 pounds of water and 200 to 215 pounds of cobs, the water to cob



UNIT FOR THE STEAM DIGESTION OF CORN COBS

FIG. 3

ratio of 4:1 is reached early in the process. Under these conditions the resulting yields were slightly improved (Table III). Run C-1 is abnormal because of the long time of digestion. Runs C-2 and C-3, however, with normal time conditions, are comparable with the runs in Tables I and II.

In order to obviate as far as possible the variation of the volume of liquid in the apparatus during the reaction period, the digester and steam line were insulated with an asbestos-magnesia covering and hot water was employed for charging. Runs D-1 and D-2 were made with this improvement, which resulted in a marked decrease in steam consumption, but with no material change in yield. A charge of 700 to 750 pounds of water at 90° C. was required to obtain the desired 4:1 ratio.

From the standpoint of time, yields, and steam consumption, the conditions given for the Experiments D-1 and D-2 (Table III) may be considered nearly optimum for the steam digestion process. The time of digestion is 2 hours. The total period from turning on the steam to discharging is 145 to 150 minutes. The charging operations require not more than 15 to 20 minutes, so that the entire cycle may be completed in less than 3 hours. The yield of furfural that may be isolated is slightly over 6 per cent (6.36 × 95 per cent = 6.04) of the air-dry weight of the cobs.

Effect of Iron on Furfural Yield—The yields of furfural of around 6 per cent obtained with the digester are decidedly lower than the maximum yield of nearly 9 per cent obtained in the laboratory under comparable conditions of time, temperature, and water-cob ratio.

Since the laboratory experiments were made in a copper autoclave while the digester was of iron, it was suspected that the difference in materials might have some effect on the results. Accordingly, the laboratory experiments were repeated under the optimum conditions. Constant results were obtained in four different runs, the yield being 8.9 per cent. When the same autoclave was provided with a sheet-iron lining, yields varying from 8.7 to 7.0 per cent were obtained. The highest yields were observed where the iron had become coated with a dark film of decomposition products and the lowest after the iron had been thoroughly cleaned.

From these laboratory experiments it is evident that the presence of iron has an adverse effect on the yield of furfural by the steam digestion process and that it would be advisable to employ a digester lined with tile or some other inert material.

Steam Consumption—The steam consumption for any run may be readily calculated from the data in the tables. Since all steam introduced into the digester is either condensed there or distilled over, the amount consumed for any particular run may be found by measuring the volume of the distillate and noting the increase of liquid in the digester during the run. Thus, for the typical case (compare Table III), where 225 pounds of cobs and 700 pounds of water at 90° C. were employed, the quantity of distillate would be 700 pounds and the increase 100 pounds, corresponding together to 800 pounds of steam.[10] Assuming that the temperature of the boiler feed water was 70° F., and the average gage pressure of the steam 145 pounds, this corresponds to approximately 925,000 B. t. u.

For the recovery of the weak furfural solution from the drained liquid to be used in a subsequent charge, about 300 pounds of solution must be distilled from the 800 pounds of discharge liquor. Assuming that it were fed to a single effect evaporator at 70° F., about 325,000 B. t. u. would be required.

For the production of furfural in the form of a 2 per cent solution with a yield of about 13.5 pounds, or 6 per cent, about 1,250,000 B. t. u. would be required, or 95,000 B. t. u. per pound of furfural. This is assuming that water used for charging the digester was heated with waste steam but with no other saving of heat in the process.

CONCENTRATION OF DILUTE FURFURAL SOLUTIONS

To utilize a continuous still the requirement of constant feed composition must be met. Since the furfural content of the digester distillate varies greatly in different parts of the run, it would not be feasible to use the uncondensed vapor as feed for the column still. A constant composition feed may be readily obtained by using the mixed condensed distillates. This procedure was adopted in the experimental plant.

Composition of Feed Liquor—The furfural concentration of the feed liquor (digester distillate) has averaged 2 to 3 per cent, although test runs with the column still have been made with concentrations varying from 0.5 per cent to over 7 per

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[10] The figures for steam are given to the nearest 50 pounds, which represents the limit of accuracy of the working conditions

TABLE III PRODUCTION OF FURFURAL USING OPTIMUM WATER-COB RATIO

Run	Weight of Charge: Cobs Lbs.	Weight of Charge: Water Lbs.	Time for Heating to 180° C. Min.	Time of Digestion Min.	Time of Blow-off (Pressure, 135-5 Lbs.) Min.	Weight of Total Distillate Lbs.	Furfural in Distillate: Concentration Per cent	Furfural in Distillate: Weight Lbs.	Discharge Liquor Lbs.	Furfural in Discharge Liquor Lbs.	Total Furfural Produced Lbs.	Yield[a] Per cent
C-1	200	540	10	160	27	1091	1.39	15.2	1027	0.8	16.0	8.00
C-2	215	600	20	120	26	887	1.47	13.0	1150	1.4	14.4	6.70
C-3	200	550	12	120	28	770	1.61	12.4	972	1.8	14.2	7.10
D-1	225	700	11	120	20	731	1.69	12.3	757	2.0	14.3	6.36
D-2	227	750	6	120	19	708	1.83	13.0	852	1.9	14.9	6.56

[a] Based on air-dry weight of cobs.

TABLE IV—OPERATING DATA WITH EXPERIMENTAL COLUMN

Conditions: Feed rate, 89 kg. per hour; product rate, 2.41 kg. per hour; steam pressure, 25 lbs. per square inch; temperature of feed, 25° C.

Fraction	Weight Per cent of Original Feed	Concentration of Components in Each Fraction (Weight per cent): Furfural	Acetaldehyde	Organic Acid (Calcd. as Acetic)	Per Cent of Original Components of Feed Liquor in Each Fraction: Furfural	Acetaldehyde	Organic Acid (Calcd. as Acetic)
Feed liquor	100	2.74	0.044	0.65	100	100	100
Heads	0.2	28	8.5	0.14	2.0	39	0.04
Product (crude furfural)	2.71	95.2	1.0	0.23	94.1	61	0.96
Discharge[a]	181	0.052	..	0.355	3.4	..	99

[a] Discharge is diluted with condensed steam. Ratio of volume discharge to volume feed liquor, 1.81:1.

cent. The acetaldehyde and methanol concentrations were calculated from analyses of the heads and crude furfural portions. All the acetaldehyde formed during the digestion process does not appear in the feed liquor, a large portion having been lost by evaporation. The following represents the amounts of constituents other than water present in the feed liquor:[11]

	Per cent
Furfural	2 to 3
Acetaldehyde	0.04 to 0.06
Methanol	0.02 to 0.04
Organic acid (as acetic)	0.6 to 1.0

The concentrations of acetaldehyde and of methanol are so low that at first glance it would seem hardly worth while to separate the heads portion from the crude furfural, and better policy to take all the vapors together from the top of the column. Experience in distilling furfural solutions, however, had shown that both the upper layer in the decanter and the lower crude furfural layer contain acetaldehyde. Its presence increases the mutual solubility of water and furfural, and when the upper layer is returned to the still the acetaldehyde concentration increases in the column until it finally prevents the separation of a furfural layer in the distillate. Hence, in order to obtain continuous decantation, the larger part of the lower boiling impurities must be separated from the furfural-water vapors in the still.

OPERATING DATA ON COLUMN STILL—The general operation of the column has been outlined along with the description of the apparatus. In commencing operation, the feed rate, steam pressure, decanter return, and dephlegmator cooling water must be carefully regulated for a half-hour or more, until a balanced condition has been obtained in the column. After that, the column will run without attention, save for the occasional checking of steam pressure and other controlling factors.

Table IV gives the operating data for a typical run with the column still, samples and readings having been taken at a time during the run when the column had been regulated to obtain nearly optimum working conditions. The composition of the feed liquor and the still products and the distribution of the original components among the various fractions are shown.

More than 94 per cent of the original furfural is found in the "crude furfural" product, and only 3.4 per cent has been lost with the discharge from the column. The difference between the sum of the furfural in the products and in the feed (0.5 per cent) is well within the limit of accuracy of the feed and product rate measurements. Approximately 99 per cent of the original organic acid, calculated as acetic, is found in the discharge from the column.

About 60 per cent of the acetaldehyde of the feed liquor is found in the crude furfural and 40 per cent in the heads. Better operating conditions in the upper portion of the column would reduce the acetaldehyde in the crude furfural product. The methanol was not determined in this run, but in another run the concentration in the heads was over 8 per cent, with only a trace present in the crude furfural.

CAPACITY OF COLUMN AND LOSS OF FURFURAL IN DISCHARGE—With any given feed rate the pressure of the open steam used for vaporizing the liquid in the column must be regulated to secure a minimum loss of furfural in the discharge liquor. If the steam pressure is too low, not all of the furfural is removed from the feed liquor in the exhausting column. If it is too high, the vapors from the plates are diluted with steam, with the result that the furfural composition in the main distillate is decreased. With the feed entering below its boiling point, as in the experimental column, a stage is reached when the feed rate and steam pressure are increased, at which the combined volumes of feed and condensed steam exceed the capacity of the overflow pipes. The effect, known as "priming," then occurs, and limits the feed rate and capacity of the column.

In calculating the quantity of furfural in the discharge, the discharge rate may be readily determined from the concentration of acetic acid. For all practical purposes, since 99 per cent of the acetic acid in the feed liquor is found in the discharge, the ratio of acetic acid concentration in the feed to that in the discharge is the reciprocal of the ratio of their volumes or rate of flow.

The effect of variations in feed rate and steam pressure on the quantity of furfural lost in the discharge is illustrated in Table V. Direct comparison can, of course, be made only between the data obtained in runs with approximately equal concentrations of feed liquor, such as Runs 2 and 3, and Runs 4 and 5. It has been possible to obtain as low a furfural loss as 0.6 per cent in the discharge with a medium feed rate, using a feed liquor containing 4 per cent of furfural.

The maximum feed rate before priming occurred was about 90 kg. per hour, giving a capacity for the column on a 2 per cent feed of 1.8 kg. of crude furfural per hour, or approximately 4 pounds. For a 3 per cent feed the maximum capacity is nearly 6 pounds of crude furfural per hour. This is calculated, considering 3 per cent of original furfural lost in the discharge and 2 per cent going into the heads portion. In practice a rate of 5 to 6 pounds of crude furfural per hour was often obtained over a period of several hours.

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[11] The distillate obtained in previous experiments from the digestion of corncobs with 10 to 30 per cent sulfuric acid differed in composition from this in containing 1 to 2 per cent of acetic acid and 0.02 to 0.04 per cent of acetone, with no acetaldehyde present, nor any appreciable amount of methanol.

TABLE V—EFFECT OF VARIATION IN FEED RATE AND STEAM PRESSURE ON LOSS OF FURFURAL IN DISCHARGE

Run	Steam Pressure Lbs./Sq. In.	Feed Rate Kg./Hr.	Acetic Acid Concentration (Normality) Feed (A)	Discharge (B)	Ratio of Discharge to Feed Rate (A/B)	Furfural Concentration Feed %	Discharge %	Proportion of Original Furfural Lost in Discharge %
1	22	67	0.106	0.053	2.0	2.30	0.023	2.0
2	22	75	0.115	0.064	1.8	2.77	0.044	2.9
3	22	86	0.118	0.064	1.8	2.71	0.100	6.6
4	20	90	0.140	0.092	1.5	3.03	0.331	16.4
5	22	90	0.140	0.092	1.5	3.03	0.229	11.3
6	25	90	0.108	0.056	1.9	2.74	0.060	4.2
7	27	90	0.152	0.076	2.0	2.88	0.039	2.7

STEAM CONSUMPTION—From the column showing ratio of discharge rate to feed rate (Table V) the steam consumption may be readily figured. A ratio of 1.8:1 to 2.0:1 may be said to be average for good separation under the conditions of the experimental plant.

Considering the typical run in Table IV where the ratio is 1.8:1, the steam consumed is 81 pounds per 100 pounds of feed. The weight of crude furfural produced is 2.71 pounds, or approximately 30 pounds of steam are used per pound of crude furfural. The temperature of the entering feed can be raised nearly to its boiling point, utilizing the heat contained in the discharge from the column. In the experimental plant, however, the temperature of the entering feed was 25° C., and about 5 pounds of steam were consumed in bringing the feed to its boiling point. The separation of 1 pound of crude furfural required 25 pounds of steam, which is, at 25 pounds gage pressure, equivalent to about 29,000 B. t. u.

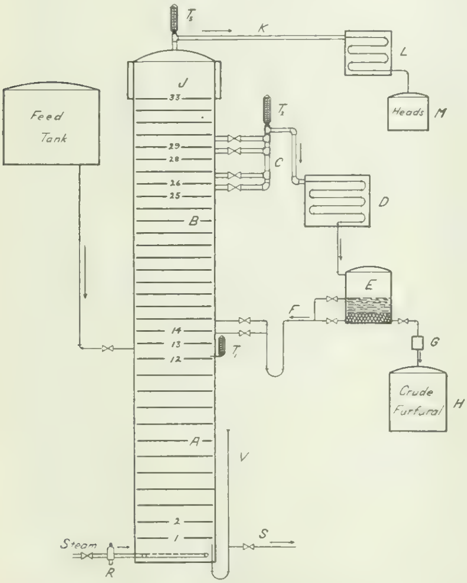

FIG. 4—DIAGRAM OF CONTINUOUS FURFURAL STILL

A = Exhausting section
B = Rectifying section
C = Main vapor pipe
D = Main condenser
E = Decanter
F = Reflux return pipe
G = Tester
H = Crude furfural receiving tank
J = Dephlegmator
K = Heads vapor pipe
L = Heads condenser
M = Heads receiving tank
R = Steam pressure regulator
S = Discharge pipe to sewer
T_1, T_2, T_3 = Thermometers
V = Vent

The reflux in the experimental still was partially provided by condensation of the vapors on the sides of the noninsulated column, with a consequent large heat loss and inefficient reflux condition. In spite of this adverse condition, the steam consumption necessary to separate furfural from its dilute solutions is very low.

COMPARISON OF EXPERIMENTAL WITH THEORETICAL COLUMN—The continuous column used was necessarily experimental in design. Since its construction, the equations developed by Lewis[12] for the rectification of binary mixtures have opened up new possibilities in the scientific design of column stills. The Lewis method has been extended to cover the conditions of rectification with continuous decantation and its application to the separation of furfural and water.[13] A comparison of the calculated and experimental data shows that the column actually used is not very efficient from the standpoint of capacity, location of feed plate, provisions for sufficient reflux, and steam consumption. However, it gives an efficient separation of components with a reasonable steam consumption.

BY-PRODUCTS AND RESIDUES

The low-boiling by-products of the steam digestion process are acetaldehyde and methanol. The yields, based on the weight of cobs, are relatively small—about 0.1 and 0.06 per cent, respectively. However, the quantity of each product is more than 8 per cent of the heads from the column still, and can be isolated while recovering the furfural from this portion.

The principal by-product of the process is the organic acid contained in the discharge liquor from the column. This acid is largely acetic, although formic acid is present in small quantities. The yield of acid is about 2 per cent of the weight of cobs, but the concentration is so low in the discharge liquor as to preclude its economical separation by the usual methods. A modification of the recent French process for recovery of acetic acid in manufacturing tanning extracts,[14] where the dilute acid is passed in vapor form through an alkaline solution, might well be applied in this case. This yield of 2 per cent represents less than one-half of the total organic acid produced in the process. The remainder is found in the residual liquor from the digester.

The cellulosic residue from the process retains about four parts of moisture which may be expelled to a large extent by pressing. For this operation a hydraulic press which delivered the material with a moisture content of about 60 per cent was used.

The weight of the dry residue from 225 pounds of cobs would be approximately 140 pounds. This material has a B. t. u. value of about 9000. The 140 pounds correspond, therefore, to 1,260,000 B. t. u. The heat value of the press cake would be decreased by an amount of heat necessary to evaporate about 200 pounds of moisture and raise the steam to the temperature of the flue gases, leaving about 1,000,000 B. t. u. for steam raising. Provided no serious difficulties were encountered in burning, the residue might furnish a substantial part of the heat requirements for the digestion process. This material has also been found suitable for certain pressed articles[15] used as substitutes for wood, wall board, etc. By treatment with caustic soda solution and washing, it may be converted into a wood-flour substitute.

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[12] THIS JOURNAL, **14**, 492 (1922).

[13] An article giving the details of this extension of the Lewis method has been submitted for publication.

[14] Depasse, *Chimie & industrie*, **7**, 244, 458 (1922).

[15] Gruber and Bashioum, U. S. Patent 1,427,378 (August 29, 1922).

The concentrated discharge liquor from which the free furfural has been expelled contains, among other substances, all the potassium originally present in the cobs. As the potassium content of the cobs is more than 0.5 per cent, under favorable conditions recovery might be profitable.

General

The plant here described has a capacity of over 100 pounds of furfural per 24-hour day, if run on a continuous basis. Its features are capable of ready enlargement to a commercial scale. The type of digesting equipment employed is similar to that used in garbage reduction plants. Large capacity may be attained by increasing the size and number of units. A continuous column still, large enough to handle all the furfural produced in a plant, can be constructed, although two columns would be preferable in a very large plant.

In the experimental plant, the operations were performed by two chemists and a helper. A plant of several times the size could be operated with little additional labor. The labor item, however, will be the main factor in the cost of producing furfural except with very large installations.

The process as developed is simple and commercially feasible. Not only corncobs, but many other pentosan-containing vegetable wastes, such as oat hulls, rice hulls, bagasse, etc., may constitute the raw material. Some of these products give very good yields of furfural, but none of them have proved equal to corncobs.

Acknowledgment

Acknowledgment is made to the E. B. Badger & Sons Company, the J. P. Devine Company, and the Vulcan Copper and Supply Company, for their coöperation in designing the column still; also to the Kutztown Foundry and Machine Company for valuable suggestions in connection with the digesting equipment. A. C. Fieldner, of the United States Bureau of Mines, furnished data on the fuel value of the cellulosic residue. The Office of Development Work of the Bureau of Chemistry has given much assistance in planning, designing, and drafting.

Nonmetallic Inclusions in Hypereutectoid Steel[1]

By **E. G. Mahin and G. B. Wilson**

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Methods already outlined in earlier papers for studying solubility effects upon ferrite separation were applied to the observation of these effects upon cementite separation in hypereutectoid steels. The results indicate that at least silicon, phosphorus, titanium, chromium, nickel, aluminium, and copper, singly or conjointly, are effective in causing premature cementite separation if these elements are themselves segregated in the steel. It would appear also that any stresses that may be set up by forcing the insert into the body steel under pressure can have no effect of this kind.

The undesirable effects of nonmetallic inclusions cannot be removed by thermal treatment, since such inclusions furnish an inexhaustible supply of contaminating material. The only remedy seems to be in refining the processes of manufacture of steel to the highest possible degree, so that steel may be produced which has a minimum of these objectionable bodies, and so that this minimum of material may be as finely divided and as widely disseminated as possible.

THE influence of foreign inclusions of a nonmetallic character upon the localization of ferrite in cooling hypoeutectoid steel has received much attention from various investigators. In four earlier papers from this laboratory,[2] this influence has been discussed from the standpoint of solubility effects, and support has been given to the view that not only is total insolubility of inclusions theoretically impossible, but that the existing slight solubility of such bodies is an important factor in the determination of the localization of ferrite.

If this theory is correct, a similar explanation should be indicated for the localization of cementite by inclusions. We are here dealing with the opposite branch of the transformation curve, in a system in which cooling austenite becomes saturated with cementite upon entering the transformation range. Similar conditions should obtain in this case. The austenite becomes saturated first at A_{cm}. Supersaturation becomes acute upon further cooling, and it is finally relieved, at Ar_{cm}, by local rejection of the solute. Normally and in austenite of uniform composition, cementite might be expected to form at boundaries and cleavage faces of austenite grains, and this is usually the case. But here, as with ferrite in hypoeutectoid steels, slight differences in carbon content and in cementite solubility—the latter due to localization of dissolved impurities—may have an influence in the determination of the locus of cementite in network formation.

In the last paper cited above[2] it was pointed out that ferrite segregation from these causes is not so noticeable or important in steels of only slightly hypoeutectoid composition, because of the narrowness of the transformation range for such steels, the entire movement of excess ferrite, across and out from the austenite grain, taking place in a comparatively short period of time. A similar statement applies to hypereutectoid steels, and, since the majority of commercial steels of this character contain carbon sufficient to form only a comparatively thin network, and rarely isolated grains except where cementite has coagulated, it follows that in most cases co-segregation of cementite and inclusions is not particularly striking or important. However, there seems little room for doubt that such co-segregation is a fact. Many metallographists have noted this,[3] and a careful examination of such steels will usually reveal cases, such as those illustrated in Fig. 1. Here, as in other similar steels, inclusions are found to be either directly in the cementite network or at an appreciable distance from it and well within the pearlite grain. That is, the directional influence of the inclusion is not sufficiently important to shift the locus of the envelope of cementite through any considerable distance, but if there is any tendency for this envelope to form in the

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[1] Received March 16, 1923. Presented before the Division of Industrial and Engineering Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] This Journal, **11**, 739 (1919); **12**, 1090, 1095 (1920); *Chem. Met. Eng.*, **27**, 980 (1922).

[3] Brueil, *J. Iron Steel Inst.* (*London*), **74**, 57 (1907); Stead, *Ibid.*, **91**, 140 (1915); Levy, *Iron Steel Inst.* (*London*), *Carnegie Schol. Mem.*, **3**, 260 (1911).

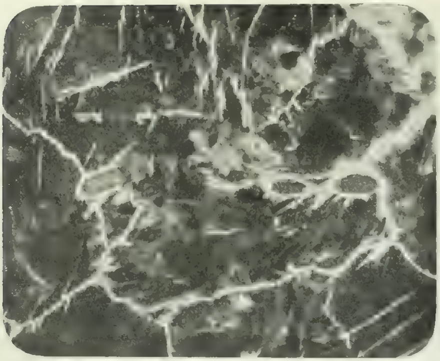

Fig. 1—Inclusions in Cementite Network. × 250

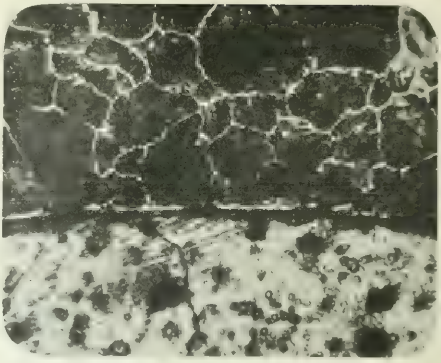

Fig. 2—Silicon Steel (below) in Hypereutectoid Body. Two Hours at 900°. × 100

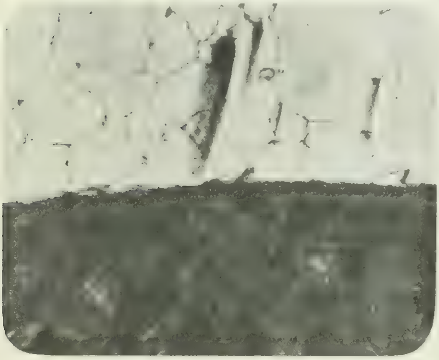

Fig. 3—Same as Fig. 2, Except Sodium Picrate Attack. × 100

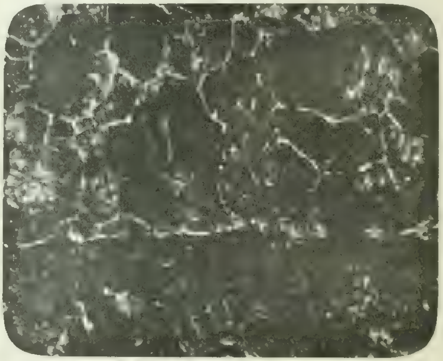

Fig. 4—Phosphorus Steel (below) in Hypereutectoid Body. Two Hours at 900°. × 100

immediate vicinity of the inclusion, the latter will be found directly in the envelope itself. There are relatively few exceptions to this rule, but this is a matter that appears not to have been fully appreciated by most metallographists who have discussed the question of inclusion influence. The occurrence of an inclusion in the body of a pearlite grain should not be regarded as exceptional unless it is found near the edge of such a grain. In a general way it may be said that the center of the austenite grain which generated the pearlite grain is highest in carbon in hypo-, and lowest in carbon in hypereutectoid steels, unless these have been normalized. The disturbing influence of the inclusion is then opposed by the natural tendency of ferrite or cementite to form at grain boundaries, and it is only when the inclusion is somewhere in the vicinity of such boundary that its influence might be expected to give any striking results.

Procedure

In the effort to determine the relative importance of solubility effects upon cementite segregation, the writers have used the general method as developed in their laboratory for studying similar effects in hypoeutectoid steels. The introduction of inclusions of the general nature of those naturally occurring in commercial steel has not appeared to be feasible, for reasons discussed in the first paper of this series. Clean, unoxidized rods of alloys and special steels were driven into freshly drilled holes of hypereutectoid steel. The composite specimen was then heated for varying periods at temperatures above the transformation range for the body steel. After furnace cooling, sections were polished and examined to determine the character of contact. They were then etched and reëxamined.

The first series of metals used as inserts consisted of specially made steels.[4] For use in this connection these steels possessed the disadvantage that they were hypoeutectoid in carbon content and, in consequence, they invariably absorbed carbon from the hypereutectoid body steel. However, the thermal treatments were continued long enough to permit more carbon to move into the zone thus impoverished, so that hypereutectoid composition was maintained in this region. Diffusion of the excess impurity of the insert into the surrounding metal might be expected to occur, as usual.

The body steel for these experiments contained the following percentages of the respective elements: carbon, 1.2; manganese, 0.30; phosphorus, 0.02; sulfur, 0.03; silicon, 0.20. In the illustrations the material of the insert occupies the lower portion in each case.

Results

Effect of Silicon—The etching treatment suitable for revealing the structure of carbon steel does not definitely etch the 4 per cent silicon steel used here. A narrow band of cemen-

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[4] This Journal, **12**, 1090 (1920).

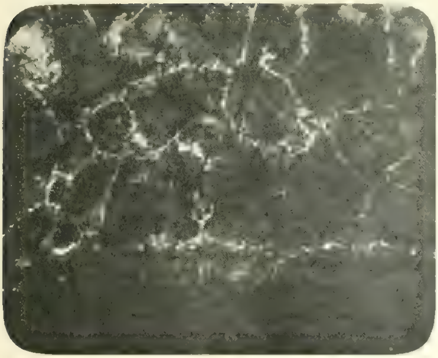

FIG. 5—TITANIUM STEEL (BELOW) IN HYPEREUTECTOID BODY, SEVENTEEN HOURS AT 900°. × 100

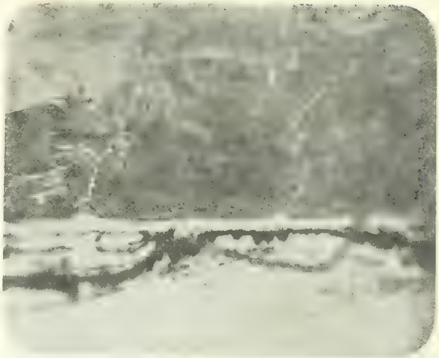

FIG. 6—CHROMEL (BELOW) IN HYPEREUTECTOID STEEL. EIGHT HOURS AT 900° × 250

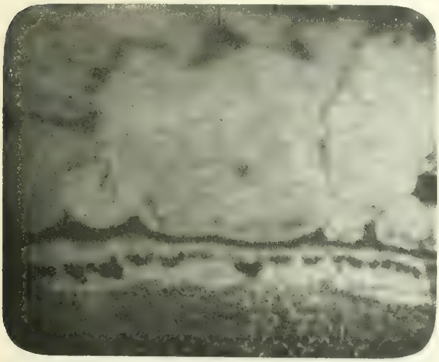

FIG. 7—SAME AS FIG. 6, EXCEPT SODIUM PICRATE ATTACK. × 250

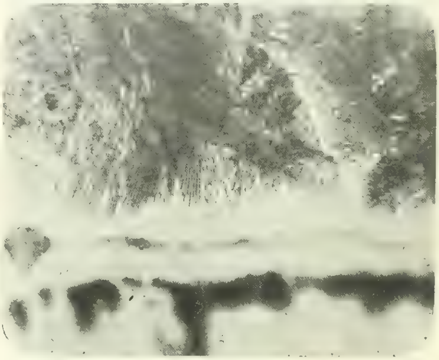

FIG. 8—ALUMEL (BELOW) IN HYPEREUTECTOID STEEL. THIRTEEN HOURS AT 900°. × 500

tite almost entirely surrounds the insert, lying just outside the line of contact (Fig. 2). That this is cementite, and not ferrite formed by decarburization by the hypoeutectoid insert, is evident from the fact that the cementite network of the body steel makes direct connection with this band. Sodium picrate confirms this conclusion (Fig. 3).

EFFECT OF PHOSPHORUS—A 1.06 per cent phosphorus steel, heated in contact with the body steel for 2 hours, produced results similar to those obtained with silicon steel, as shown in Fig. 4. Here again the bright ring joins the cementite network, which proves its hypereutectoid character.

Longer heating entirely removes this effect through extensive dissemination of the previously localized phosphorus. After 13 hours of heating at 900° to 1000° C. it becomes almost impossible to find the line of contact between the two pieces. Carbon distribution has become uniform and there is now no sharp dividing line between high and low-phosphorus areas, so that cementite separation is not now locally affected.

EFFECT OF TITANIUM—Ordinary thermal treatment of a composite specimen containing a titanium steel, as the insert, showed no effect of the latter upon cementite separation. After heating for 17 hours at 900° to 1000° C., slight cementite localization was noticeable (Fig. 5). This lack of pronounced effect is therefore apparently due to the slowness with which titanium migrates in the heated steel.

EFFECT OF CHROMIUM AND NICKEL—An insert of chromel (an alloy of chromium and nickel) was used. Figs. 6 and 7, showing the heat-treated specimen as etched with nitric acid and sodium picrate, respectively, indicate the action of these two metals, when used together in these proportions. As was noted in the discussion of the action of silicon, the cementite network directly joins the band surrounding the insert.

EFFECT OF ALUMINIUM AND NICKEL—An insert of alumel, a nickel-aluminium alloy, was used. Fig. 8 shows a broad band of unetched material, joining the cementite plates of the pearlite grains as well as the network without. Sodium picrate colors the carbide plates of the pearlite grains slightly and the network more deeply, as usual. The bright border material is not colored appreciably in 20 minutes application of the boiling picrate solution, the red line of the cementite network running into and joining this. One might conclude from this that the broad, bright band is either (*a*) austenite, retained in the cooled system through the action of nickel in retarding the transformation, or (*b*) a high nickel (and aluminium) solution of nickel or nickel carbide in cementite, the nickel inhibiting the action of sodium picrate. The first assumption is rendered unacceptable by the conclusion that if austenite has remained in the zone immediately adjacent to the contact line, it should shade into martensite and troostite in the low-nickel areas. Instead of this, the band appears to be continuous with carbide plates of pearlite grains. Hypothesis (*b*) has therefore been provisionally adopted. This view is further strengthened by the fact that a shorter thermal treatment gives a narrow band which is colored by sodium picrate, as shown in Fig. 9.

EFFECT OF NICKEL AND COPPER—An insert of constantan (copper, 53.4; nickel 45.0; other metals, mostly iron, 1.6) was used with the same stock hypereutectoid steel. The thermal treatment of the composite specimen gave a very interesting result. Apparently on account of the unusual ability of this alloy to absorb carbon, the insert has exerted a pronounced decarburizing effect upon the body piece. The movement of carbon into the insert was so rapid as to leave a wide zone of hypoeutectoid steel surrounding the insert. At the same time copper and nickel may be assumed to have diffused into the body steel, causing premature ferrite separation as usual, so that during cooling through the transformation range a perfectly even and definite ring of entirely decarburized iron-nickel-copper alloy is produced, outside of which lies a still wider, but less definite, diminishing zone of hypoeutectoid steel. Apparently, the inner band of carbonless alloy marks the limit of advance of the invading nickel-copper, while the ferrite-pearlite zone lying outside this is the result only of carbon absorption by the insert. Still farther out this merges with a zone of eutectoid steel and, surrounding the whole, the original hypereutectoid body, practically unaffected by migration of either carbon or foreign metal. These effects are illustrated in Fig. 10, although the outer, high-carbon zone was not included in the photomicrograph from which this figure was made.

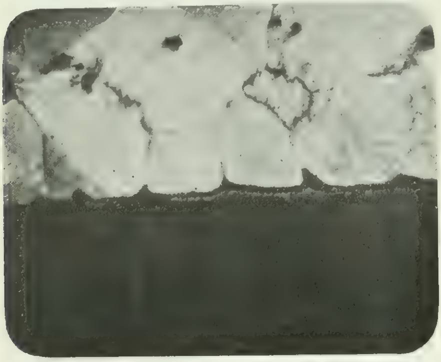

FIG. 9 ALUMEL (BELOW) IN HYPEREUTECTOID STEEL. SEVEN HOURS AT 900° SODIUM PICRATE ATTACK. × 250

It might be concluded that traces of surface impurities may have had something to do with both ferrite and cementite segregation. In some cases a slight secondary recession of carbon from the contact line in both directions has been noticed, this being independent of the more definite and pronounced action of the larger impurity. It has been only in those cases where a rather definite and unmistakable line of either constituent has been produced that the writers have felt justified in attributing the action to the foreign matter artificially introduced as an essential part of the insert itself. The general conclusion as to solubility effects is strengthened by such results for they indicate that mere surface "dirt," heated in contact with steel, dissolves in the steel to an extent sufficient to cause premature transformation at Ar_3 or Ar_{cm}, and thus segregation.

OTHER EXPERIMENTS

A number of other special steels and alloys, used in this way, gave no definite results. Whether this was due to the slowness of diffusion of the foreign element or to the absence of any effect of the invading element upon cementite solubility, cannot be stated at present. Work is still in progress.

While the use of alloys in this manner leaves one in doubt as to which element of the alloy is most active in promoting segregation of excess solute from the solid solution, the general conclusion as to the qualitative fact is not affected. From all their experiments with such alloys in both low and high carbon steel, the writers feel warranted in stating that alloys are, in general, more active than single metals in this respect.

EFFECT OF STRAIN

On account of the fact that all inserts were forced into the body steels (both hypo- and hypereutectoid) by hammering, the possibility that ferrite or cementite segregation may have been caused partly by the resulting pressure should be considered. Theoretical considerations, as well as experimental results, lead us to believe that such pressure had no effect of this kind. The separation of both ferrite and cementite from cooling austenite is accompanied by pronounced dilatation. The effect of pressure upon the system would therefore necessarily be to hinder or retard, rather than to aid, the separation of these excess solutes in the zone about the insert. In order to make a practical test of the question, inserts were made of the same material as that of the body and the composites were treated in the way already described for other specimens. In some of these cases a slight tendency toward such separation was noticed, but in the most carefully cleaned pieces it was extremely difficult to find the line of contact between insert and body after the heating, the pieces being perfectly welded together.

It may be observed also, in this connection, that the long heating that was applied to all these specimens should have given ample opportunity for all internal stresses to be relieved, as well as for the disappearance of all essential differences in grain size, the latter possibly being due to the presence of a narrow ring of deformed metal in contact with the insert. That these differences did disappear in all cases is evident from an inspection of the photomicrographs.

CONCLUSIONS

The logical conclusion from all this work appears to be that in any class of steel, excluding the one special case of steel of eutectoid composition, segregation of any dissolved constituent will have an effect upon carbon distribution in all but quenched steel, if indeed this case is to be excepted. This will apply to the ordinary four elements occurring in small quantity in all carbon steel, as well as to metallic or nonmetallic elements intentionally added in the manufacture of special steels. It will apply also to those sources of constant contamination known as nonmetallic inclusions, and with this addition—that while ordinary segregation of totally dissolved elements can be nearly or entirely cured by thermal treatment and, to some extent, by forging, no amount of either forging or thermal treatment that is possible in practice will serve to cure the evil effects of the nonmetallic inclusion, since the relatively large amount of material so concentrated and the relatively small solubility of this material in the solid solution surrounding it, make its exhaustion by diffusion a practical impossibility.

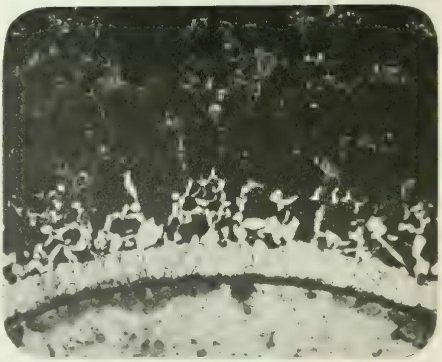

FIG. 10—HYPEREUTECTOID STEEL WITH CONSTANTAN INSERT (BELOW). TWO HOURS AT 900°. × 100

The Spectrophotometric Identification of Dyes[1,2]

I—Acid Dyes of the Patent Blue Type

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The degree in which the intensity of the absorption of solutions of dyes is modified by variations in concentration, solvent, alkalinity, acidity, and other conditions, is dependent upon the degree of alteration of the dye in molecular form or aggregation, which, in turn, is conditioned upon constitutional differences. The quantitative measurement of intensity of absorption under such variation in conditions, accordingly, affords spectrophotometric ratios, or constants, which have important diagnostic value for purposes of identification.

An analytical scheme for the identification of acid blues of the Patent Blue type is outlined, in which such spectrophotometric ratios are employed to supplement the spectroscopic data customarily obtained. A comprehensive table of constants for the identification of the dyes in question is supplied.

BY MEANS of the spectro-analytical methods and the spectroscopic data supplied by Formánek and Grandmougin,[3] it is possible to identify with comparative ease and moderate certainty the majority of dyes which were marketed prior to those years. Their general scheme of spectroscopic identification has a wide range of effectiveness, affording, in some instances, a satisfactory differentiation between dyes which may hardly be identified by other means.

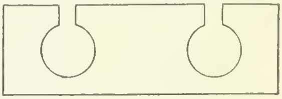
Although the general value of their methods is beyond question, it is necessary to admit that they do not invariably supply a satisfactory means of distinguishing between closely related dyes, and that the need for a more adequate basis of identification is becoming more evident each year with the increasing multiplicity of such products upon the market. Justification for the present investigation is found in a recognition of that necessity and in a belief that the earlier investigators in the field have neglected to make full utilization of certain aspects of absorption, either through a failure to realize their value as an aid in identification or because suitable instruments for their quantitative study were not available.

In the analytical scheme of Formánek and Grandmougin great emphasis is placed upon the diagnostic value of precise determinations of the spectral locations of the maxima of the absorption bands of solutions of the dyes in various solvents, a particular wherein exact measurement is a matter of extreme difficulty. On the other hand, various phenomena involving modification in the form or intensity of the absorption, which may be of equal or more important significance, are utilized only in a qualitative and incomplete degree which greatly impairs the value which the methods would otherwise possess. The failure to supply a quantitative record of such modifications in absorption is, furthermore, a serious defect which operates to limit the utility of the methods in the hands of the inexperienced analyst.

The present investigation was undertaken as a test of the effectiveness and limitations of an improved scheme of spectrophotometric identification, which, it was believed, would be free from the more serious of these objections. It was proposed to investigate the spectroscopic behavior of dyes in a quantitative manner by means of the spectrophotometer, with the expectation that it would be possible to obtain a series of spectroscopic and spectrophotometric constants which would be found susceptible of correlation with structural differences and characteristics of the individual dyes. Such constants would afford a definite mathematical expression of the essential properties of the dyes.

The Patent Blues, Xylene Blues, and Alphazurines were selected as comprising a group of dyes offering such difficulty in identification as to afford a satisfactory test of the proposed scheme, while various other acid blues of similar general type were included to render the data more complete. The samples examined were those of the ordinary commercial product as supplied to the textile trades, with the exception of one sample of Alphazurine A, which was manufactured and purified with great care and was, accordingly, of a higher grade of purity. The chemical structure of the pre-war products may be ascertained by reference to the "Farbstofftabellen" of Schultz. Of the American products Pontacyl Brilliant Blue A and Alphazurine FG are chemically identical, respectively, with Xylene Blue AS and Erioglaucine A; while Alphazurine A and Alphazurine 2 G are dyes, respectively, of the Blue A and Blue V types, in the manufacture of which the distinctive intermediate is 2,5-disulfobenzaldehyde.

A Hilger wave length spectrometer equipped with a Nutting photometer, a type of instrument combining good accuracy with great convenience in operation, was employed. One-centimeter cells were used in all measurements except those carried out with comparatively concentrated aqueous solutions. Suitable thin cells for the latter solutions are easily constructed by cementing to a microscope slide a thin sheet of mica cut in the form indicated in the accompanying diagram. In operation a thin layer of petrolatum is applied to the free surface of the mica, a second slide placed thereon, and the cell completed by tightly winding the central and outer portions with rubber bands. The subsequent introduction of the solution is easily effected. In the case of cells of the thickness employed in the present investigation (0.0432 cm.) it is possible, with a little practice in manipulation, to reduce the variation in thickness of the solution layer to within negligible limits.



Stock solutions of the dyes were prepared by dissolving 0.25 gram of dye in 250 cc. of distilled water, from which all the solutions required were obtained by appropriate dilution. In the study of the influence of alkalinity it was considered advisable to defer the addition of the alkali until the solution had been diluted to nearly its final volume, and to carry out the measurements immediately after the completion of the dilution. With the alcoholic solutions the alcohol content was made approximately 91 per cent in all instances, although it was found that an appreciable variation

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[1] Received March 1, 1923. Presented before the Division of Dye Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Contribution No. 72 from the Color Laboratory, Bureau of Chemistry, Washington, D. C.

[3] "Untersuchung und Nachweis organischer Farbstoffe auf spektroskopischem Wege," published in final form in 1908, 1911, and 1913.

in that respect was required to influence the measurements in any particular.

The general procedure followed consisted in the measurement of the absorption of the dyes throughout the visible spectrum, with such variation in concentration, solvent, alkalinity, or acidity as was necessary to define characteristic differences in behavior. It was found, however, that the complete measurement of the absorption of the dyes investigated afforded relatively little of essential value which could not be obtained merely by means of the determination of the spectral location of the absorption maxima and by the measurement of the magnitude of the absorption at that point.

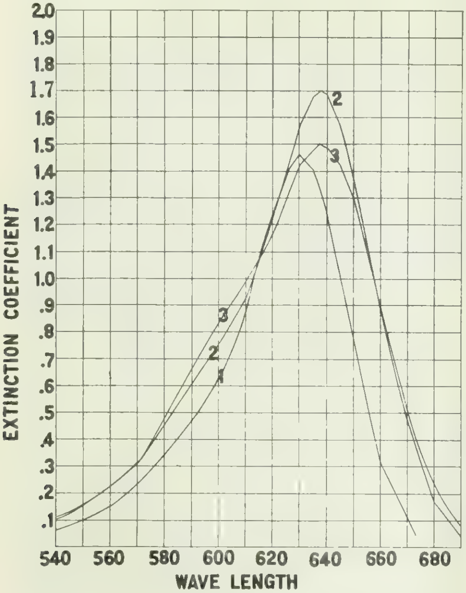

Fig. 1

Curve 1 = 30 parts Pontacyl Brilliant Blue A per million parts 92 per cent alcohol (1.002 cm. layer)

Curve 2 = 40 parts Pontacyl Brilliant Blue A per million parts water (1.002 cm. layer)

Curve 3 = 1000 parts Pontacyl Brilliant Blue A per million parts water (0.432 cm. layer)

Influence of Concentration and Solvent

The general character and degree of modification of the absorption of the group of dyes under investigation with change in concentration of aqueous solution and with change from aqueous to organic solvent, is illustrated by the absorption curves for Pontacyl Brilliant Blue A recorded in Fig. 1. With change of concentration of aqueous solutions there occurs no decided alteration in the form of the curve. It is evident, however, that the dye does not conform to Beer's law[4] over the range in concentration employed, but that with increasing dilution there is an increase in the relative magnitude of the absorption, as measured by the intensity of absorption at the maximum. It is further evident that this phenomenon is accompanied by two types of minor modification in the form of the curve. With increasing dilution there occurs a symmetrical narrowing of the curve in proportion to its height, while an unsymmetrical development or "hump," which may be observed in concentrated solutions in the region of 600 $\mu\mu$, disappears in large measure. The maximum intensity of absorption—in proportion to dye present—is found in the alcoholic solution, the curve of which shows no indication of a hump and is narrower and steeper than the curves of aqueous solutions.

It is believed by the writer that the symmetrical broadening of the absorption curves which occurs in passing from alcoholic to aqueous solution and becomes more pronounced with increasing concentration in the latter, may be accepted as evidence of an increasing degree of molecular association of the dye, while the local hump at about 600$\mu\mu$ is unquestionably an incipient modification of the general type which has been previously reported by the writer,[5] and which is held by him to connote radical intramolecular rearrangement. The degree of decrease in relative magnitude of absorption in passage from alcoholic to dilute aqueous solution, and from the latter to concentrated aqueous solution, constitutes a measure of the degree in which the phenomena referred to take place.

The data which were obtained with change of concentration and of solvent, and which would appear to be of service for the purposes in view, are given in the following table of constants (p. 836). The values recorded in Columns 1 to 5 are the following:

1—The approximate spectral location (in millimicrons) of the absorption maximum in aqueous solution.

2—The same value for alcoholic solutions of approximately 91 per cent alcoholic content.

3—The ratio of the magnitude of absorption at the maximum in concentrated aqueous solution to that in dilute aqueous solution.

4—The ratio of the magnitude of absorption at the maximum in dilute aqueous solution to that in dilute alcoholic solution.

5—The ratio of the magnitude of absorption at the maximum in concentrated aqueous solution to that in dilute alcoholic solution.

The term "dilute solution" is applied to solutions of such strength as will confine their absorption within the limits wherein accurate measurement is possible when examined with the spectrophotometer in 1-cm. layers. The concentrated aqueous solutions contained twenty-five times as much dye as the corresponding dilute solutions. (The employment of still more concentrated solutions was considered inadvisable because of the serious effect which even minute variations in the thickness of layer would have upon the accuracy of measurements in the extremely thin cells which would be required.)

It was not attempted to define the location of the absorption maxima with great accuracy. It is necessary to recognize that commercial dyes are not pure products and that minor variation in absorption may be expected between the output of different manufacturers. There is, furthermore, a definite limitation to the degree of precision with which it is possible to locate the maxima of absorption bands, and the results obtained by different investigators will be affected by the instrument employed and by variations in technic. In the case of the dyes employed in the present investigation, there will be found to be an average discrepancy of approximately two millimicrons between the locations of absorption maxima supplied by Formánek and Grandmougin[3] and those supplied by Mulliken,[6] although the same methods of examination and type of instrument were utilized in their determination.

The values recorded in the table for the locations of the absorption maxima are to be considered, accordingly, as approximations from which a minor degree of divergence is without significance. It will be seen that they have slight value in differentiating between the first six color types listed, which comprise the group of dyes under more immediate consideration. The resort to other solvents is without decided utility with these dyes, and in general merely results in a shift in absorption which is of about the same magnitude in all instances. Alphazurine FG and Cyanole Extra, among the dyes of secondary interest in the present investigation, constitute exceptions to this rule, having their maxima only slightly displaced by a change from aqueous to alcoholic solution.

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[4] *Pogg. Ann.*, **86**, 78 (1852).

[5] "The Influence of Variation in Concentration on the Absorption Spectra of Solutions of Dyes." Presented before the Division of Dye Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[6] "Identification of Pure Organic Compounds," Vol. III, **1910**.

The various absorption ratios recorded are also of slight value in distinguishing between the individual members of the group studied, although there is reason to believe that similar ratios would prove of important service in that respect with certain other groups of dyes. However, they afford a decisive differentiation between the two general types of amino substitution involved, clearly distinguishing the di-alkyl derivatives from the alkyl-benzyl derivatives. They will also prove of value in distinguishing the dyes under investigation as a class from other blues of different constitutional types.

INFLUENCE OF ALKALINITY

The dyes of the group investigated undergo two types of modification in absorption under the influence of alkalies. With certain individual dyes an appreciable displacement of the absorption band occurs, while alterations in intensity of absorption take place, in general, which are dependent upon the nature and concentration of the alkali and may require a considerable period of time for completion. The immediate effect of the presence of 0.1 per cent of sodium hydroxide may be that of increasing or of decreasing the magnitude of the absorption, depending upon the dye concerned, while that effect is followed by a gradual decrease in absorption, of which the rate and extent also vary with the individual dyes.

Since the displacement of the absorption is always encountered with those dyes which contain a hydroxyl group and is not observed with other dyes, it may clearly be attributed to a reaction of that group with the alkali. The nature of the gradual decrease in absorption which is observed in the alkaline solutions of all the dyes studied, appears to be complex. It seems probable that a progressive and extensive process of association of solute molecules accompanies the conversion of the dye into carbinol form and contributes to the loss in absorption observed.

The data included in the table of constants were obtained with solutions containing 0.1 per cent of sodium hydroxide. The values recorded are as follows:

6—The approximate spectral location of the absorption maximum.
7—The ratio of the magnitude of the absorption of the freshly prepared alkaline solution to that of a neutral solution of corresponding dye content.
8—The same ratio after the alkaline solution has stood 20 hours.
9—The same ratio after the alkaline solution has stood 5 days.

The appreciable displacement of the absorption maxima of alkaline solutions of Patent Blue A, Patent Blue V, and Cyanole Extra has decisive value for the identification of those dyes.

The immediate effect of alkalinity upon the magnitude of the absorption is of no considerable practical importance. On the other hand, it will be seen that the stability of absorption under alkaline conditions is intimately related to constitutional differences in the dyes and influenced, to an appreciable extent, not only by the two general types of substitution within the amino group, but also by the three general types of substitution within the nonaminated nucleus. The constants obtained, accordingly, are characteristic in a considerable measure of the individual dyes. The differentiation between Alphazurine 2G and Xylene Blue VS which they render possible is of particular utility in view of the close similarity of behavior of those dyes under the influence of other agents.

INFLUENCE OF ACIDITY

The effect of the presence of acids upon the absorption of the dyes investigated is illustrated by the curves recorded for Pontacyl Brilliant Blue A in Fig. 2. To the eye, the color of solutions of the dyes passes with increasing acidity from blue through green to yellow. The spectroscope reveals the fact that a yellow compound with absorption in the violet portion of the spectrum is progressively formed at the expense of the original blue compound and renders it possible to follow the transition in a quantitative manner. The determination of the magnitude of residual absorption of the original blue dye affords a measure of the degree of transition under any definite condition of acidity. It is generally held that the alteration in color under discussion is consequent upon the direct addition of acid to the amino nitrogen atoms, the valency of which increases from three to five.

The values listed in the table of constants are ratios of the residual absorption of the dyes under various degrees of acidity to the absorption of neutral solutions of a corresponding dye content. The acid conditions for which the constants were obtained were as follows:

10—Two per cent sulfuric acid (95 per cent).
11—One per cent sulfuric acid (95 per cent).
12—One-tenth per cent sulfuric acid (95 per cent).
13—Two per cent acetic acid (99.5 per cent).

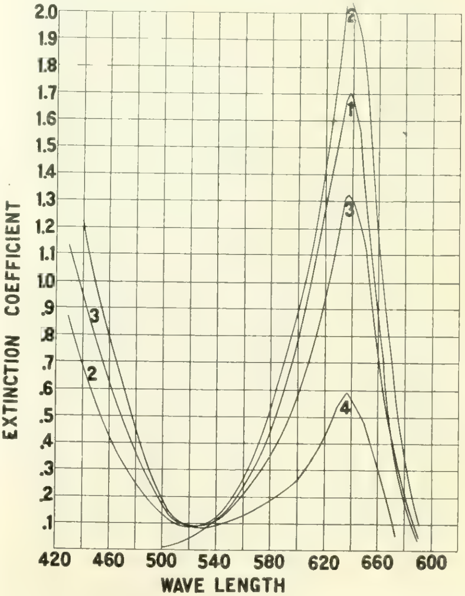

FIG. 2

Curve 1 = 40 parts Pontacyl Brilliant Blue A per million parts water
Curve 2 = 100 parts Pontacyl Brilliant Blue A per million parts 1 per cent H_2SO_4
Curve 3 = 100 parts Pontacyl Brilliant Blue A per million parts 2 per cent H_2SO_4
Curve 4 = 100 parts Pontacyl Brilliant Blue A per million parts 4 per cent H_2SO_4

TABLE I

SAMPLE	(1) μμ	(2) μμ	(3)	(4)	(5)	(6) μμ	(7)	(8)	(9)	(10)	(11)	(12)	(13)
Patent Blue A	637.5	630(+)	0.742	0.878	0.650	627.5	1.120	1.003	0.574	0.293	0.470	0.760	0.999
Patent Blue A (Berlin)	637.5	631	0.772	0.869	0.671	627.5	1.106	1.003	0.561	0.298	0.474	0.727	0.957
Patent Blue A (H)	637.5	630	0.774	0.823	0.637	627.5	1.175	1.060	0.608	0.313	0.449	0.722	0.992
Patent Blue A, Average	637.5	630(+)	0.763	0.857	0.653	627.5	1.137	1.022	0.581	0.301	0.464	0.736	0.966
Neptune Blue BG (B)	637.5	630	0.995	0.931	0.926	628.8	1.048	1.043	0.867	Trace	>0.01	0.046	0.471
Patent Blue Superfine (H)	637.5	630	0.973	0.931	0.918	627.5	1.028	0.997	0.874	Trace	>0.01	0.040	0.429
Patent Blue N (H)	637.5	630	0.992	0.910	0.902	628.8	1.033	0.999	0.854	Trace	>0.01	0.042	0.428
Patent Blue V (H)	637.5	630	0.959	0.892	0.892	627.5	1.170	1.014	0.815	Trace	>0.01	0.049	0.446
Patent Blue V, Average	637.5	630	0.980	0.925	0.910	627.5(+)	1.093	1.013	0.853	Trace	>0.01	0.044	0.444
Alphazurine A (Nat.) Textile Dye	637.5(−)	630	0.763	0.911	0.697	637.5(−)	0.964	0.508	>0.01	0.252	0.430	0.754	0.983
Alphazurine A (Nat.) Special Dye	637.5	630	0.781	0.880	0.690	637.5	0.999	0.516	>0.01	0.234	0.424	0.720	0.973
Alphazurine A (Nat.), Average	637.5(−)	630	0.772	0.896	0.694	637.5(−)	0.982	0.512	>0.01	0.243	0.427	0.737	0.978
Pontacyl Brilliant Blue A (duP)	637.5	630	0.787	0.839	0.664	637.5	0.960	0.516	>0.01	0.312	0.495	0.768	0.989
Xylene Blue AS (S)	637.5	630	0.789	0.832	0.657	637.5	0.937	0.558	>0.01	0.317	0.495	0.789	0.979
Xylene Blue AS, Average	637.5	630	0.788	0.836	0.660	637.5	0.949	0.537	>0.01	0.315	0.495	0.779	0.984
Xylene Blue VS (S)	640	632.5	0.973	0.918	0.900	640	0.993	0.819	0.206	Trace	>0.01	0.041	0.445
Alphazurine 2G (Nat.)	640	631.3	0.958	0.939	0.892	638.8	0.988	0.858	0.337	Trace	>0.01	0.039	0.399
Alphazurine FG (Nat.)	630	628.8	0.807	0.984	0.801	630	0.970	0.587	>0.01	0.369	0.526	0.733	0.929
Cyanole Extra (C)	612.5	611.3	0.951	0.834	0.792	606.3	0.980	0.766	0.340	0.01	0.070	0.291	0.873
New Patent Blue B (By)	625	617.5	0.909	0.932	0.846	625	0.976	0.640	24.1	0.068	0.141	0.435	0.884
New Patent Blue 4B (By)	615	608.8	0.969	0.841	0.816	615	0.963	0.626	11.1	0.059	0.147	.458	0.854

The stability of the dyes to acid conditions is also closely related to structural differences. The influence of the type of substitution at the amino nitrogen is extremely well defined. Although the effect of variation in the type of nonaminated nuclear structure is relatively very much less clearly evident, the extremes of acidity employed develop sufficient differences to indicate a definite relationship. In the instances of Alphazurine A and Xylene Blue AS, the effect of 2 per cent of sulfuric acid is sufficiently distinctive to afford a means of decisive differentiation which is the more valuable because the dyes in question exhibit but slight dissimilarity in general behavior.

In Table I all the constants obtained are recorded. All values are averages of two or more series of determinations in which a substantial agreement in results was obtained.

This table constitutes a chart wherein various significant characteristics in the behavior of the individual dyes, which clearly originate in structural differences, have been recorded in definite spectrophotometric terms. Any of the constants utilized may be obtained with relative ease and substantial accuracy by means of any modern type of spectrophotometer, while the fact that the majority of them are ratios serves to render the reliability with which they may be determined independent, in large measure, of differences in the type of instrument employed and in the technic and skill of the observer.

The various constants recorded do not possess equal diagnostic value, and it will be unnecessary to carry out the entire series of measurements in order to arrive at a comparatively positive identification. The mere determination of the location of the absorption maximum in aqueous solution will be sufficient to distinguish the members of the series of the first six color types listed from the dyes of similar general type included in the tables. For the purpose of differentiating between the first six color types, it is recommended that the next step be that of the determination of the relative magnitude of absorption in neutral solution and in the presence of 2 per cent of sulfuric acid. The value obtained will not only serve to indicate unmistakably the character of the substitution in the amino group, but will further suffice to distinguish between Alphazurine A and the remaining dyes of similar constitution as regards the nonaminated nuclei. The determination of the location of the absorption maximum in alkaline solution will then definitely establish the presence or absence of the Patent Blue type of nonaminated nucleus. It may then remain necessary to distinguish between Xylene Blue VS and Alphazurine 2G. The absorption of the dye in 2 per cent acetic acid will afford immediate evidence of value which should, however, be corroborated by the determination of the degree of stability to alkaline conditions. The determination of further constants may be considered unnecessary, but will be of advantage in confirming the preliminary verdict and eliminating the possibility of error.

Although it is held by the writer that the scheme of identification outlined has been shown to be effective and may be accepted for application with the dyes investigated without reservation in any essential respect, it is considered advisable to qualify the recommendation of its adoption in certain minor respects.

The variation in commercial dyes is such that the determination of exact and unvarying constants of any character for a given color type is not possible. It would be necessary for that reason alone to recommend that identification be based upon substantial agreement in respect to all significant factors, making allowance for a moderate degree of variation in individual values.

It was further noted, in the course of the present investigation, that minor discrepancies occurred in duplicate absorption measurements in neutral solvents, which are apparently to be attributed to variations in hydrogen-ion concentration, while evidence was obtained that variation in temperature may have an appreciable influence upon the stability of absorption under alkaline conditions. It is recognized, accordingly, that it would be desirable to modify the procedure to the extent of making provision for a regulation of those factors, and that that course might render it necessary to revise certain of the constants which have been obtained under less definite conditions. Pending such revision of technic and of constants, it may be advisable for the analyst to verify the agreement of the sample under investigation with the color type to which he has assigned it by means of parallel determinations of values with a sample of the latter of known identity if it is available. It is believed, however, that the differences upon which identification has been based are so considerable, and that the influence of any probable variation in working conditions upon any of the constants which are essential to the scheme of identification will be so slight, that the methods outlined and the data supplied will serve to render possible the certain identification of any of the dyes investigated, even by an analyst who may not have access to samples of known identity for purposes of direct comparison.

The general principles of identification employed in the present investigation may be expected to be found susceptible of extensive application. Other types of dyes which offer difficulties in identification will be investigated along similar lines as opportunity is afforded.

ACKNOWLEDGMENT

Acknowledgment is due to E. I. du Pont de Nemours & Company for samples of Pontacyl Brilliant Blue A and of various pre-war dyes, and to the National Aniline & Chemical Company for samples of the Alphazurines.

The Use of Dyes as Temperature Indicators[1]

By Paul A. Kober

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A brief outline is given of a reliable and efficient method for checking temperatures in heating processes. The disappearance of or the change in color indicates that the part to which the color has been applied has actually received a definite amount of heat.

The method provides a simple and inexpensive means for temperature checks on an entire factory production. Its application in a few cases is given.

In MANY industries baking or heating constitutes an important part of manufacturing processes. These are necessary to bring about some desired physical or chemical change, and in most cases it is essential that the amount of heat applied comes within certain fixed limits, since quality and production are dependent upon it. The amount of heat applied is usually determined by the time of heating and temperature, the latter being indicated by the more common methods of pyrometry. In many cases, however, the methods used do not indicate the actual temperature conditions sought, and where a large production is involved are often costly both as to loss of time and material.

A method recently developed for this purpose, based on the decomposition of an organic dye, has proved to be a very reliable and efficient heat indicator. The absence or presence of the color on or in the heated product to which it is applied determines accurately whether or not the product has received a definite amount of heat. Some of the essential considerations in the use of dyes as heat indicators and a few of its applications will form the basis of this paper.

Temperature Indicator Requirements of Dyes

In order that a dye may act as a heat indicator, it is necessary that when heated it break down readily into gases and leave no appreciable residue behind. Most dyes on heating do not possess this characteristic. Usually they decompose to some extent into other solid substances and then disappear only after a high temperature has been applied, thus carbonizing the dye with subsequent oxidation. There are, however, a considerable number of dyes which act as very good indicators when subjected to heat. These break down easily with the complete disappearance of the color. Dyes which change on heating through many shades will obviously not act as good indicators. Colors such as blue, green, and red, when applied to various substances, act as the best indicators, while colors like yellow and brown show insufficient color changes. Dyes that break down readily on heating are not confined to any particular chemical group. Most of those found, however, are identified with the triphenylmethane group of coloring matters.

The disappearance of a dye, or its complete decomposition into gases, is a function of the time of heating as well as of the temperature. Unlike a melting point salt, which indicates a definite temperature regardless of the time element, a dye will completely disappear at various time intervals and temperatures. Aside from these two factors the disappearance of a dye is also a function of the amount of dye applied to the substance. The heat which causes a dye to break down is conveyed to the dye by both convection and conduction of the material to which it is applied. For all practical purposes it may be safely assumed that when the dye disappears the part to which it is applied has absorbed a definite amount of heat. It will be apparent that a dye cannot indicate any particular temperature, but acts only as an indicator of the amount of heat applied to the part measured.

Dyes which act as indicators differ in temperature and time interval of disappearance, all other factors being constant. In the accompanying figure curves are given of indicators showing the relation between temperature and time of disappearance. These values were obtained by inserting glass rods, on which a thin coating of the dye was applied, into an oven held at constant temperature, and noting the time when the color had entirely disappeared. The curves show only the approximate relative values of the different dyes. The time of disappearance for the higher temperatures may vary in any particular test according to the mass and heat capacity of the substance on which the color is applied. It will be noted from accompanying curves that all the dyes function about the same, the curves being parabolic. The indicators represented in Fig. 1, with their relative time of disappearance when subjected to constant oven temperatures, are given in the following table:

Dye	Approximate Time of Disappearance at 350° C. Min.	Approximate Time of Disappearance at 375° C. Min.	Temperature of Dye Designated by Melting Point Salt ° C.
Malachite green	3/5	1/2	220
Methyl violet	4/5	3/4	250
Chemco red	1	5/8	280
Chemco blue	1 1/2	1 1/5	310
C. P. 196 (red)	4 3/4	2 1/4	370
Erythrosin	60	6 1/4	390

Aside from showing the relations of the various dyes by curves, they may also be designated by some specific temperature. This may be done by comparing a dye with a melting point salt which just melts when a certain dye just disappears under the same conditions. The dye may then be designated by the melting point of the salt. The temperatures given in last column of the table are so designated.

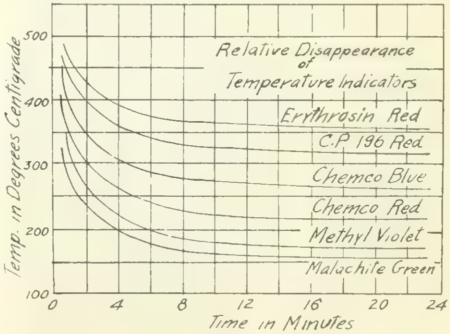

Fig. 1

Application of Dyes as Indicators

In the application of dyes as heat indicators three methods may be employed depending on the conditions of heating:

(*a*) Applying a thin film or coating by means of a standard solution to the part to be heated.

(*b*) Mixing a standard solution of a suitable dye to compounds or mixtures to be baked.

(*c*) Applying the proper dye on a test plate, which, with the product to be measured, is subjected to the same heating conditions.

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[1] Received February 15, 1923.

To obtain consistent results it is necessary to make up standard solutions whose purity and tinctorial power are known. Absolute alcohol (either ethyl or methyl) has been found best as a solvent. The presence of water will cause some dyes to hydrolyze and others to combine with one another, thus destroying their temperature-indicating properties. All dye solutions should be filtered before using to eliminate solid matters and gums. The concentration of the dye solution will depend on whether it is to be added to a mixture, as in a cement, or applied to some surface. In the former case the concentration will determine to some extent the time of disappearance, while in the latter the varying concentration which is likely to be applied to any surface will not appreciably vary the time of disappearance. It is, however, desirable for surface use to make the concentration as low as possible, yet high enough to give sufficient tinctorial power. Where an excess amount of dye is applied to any surface there is a tendency for a slight smudge to remain.

Double Indicators

In order to indicate in heating processes whether the heat applied has passed a maximum as well as a minimum temperature limit, two suitable indicators would ordinarily be necessary. To avoid the application of two different dyes, an indicator was developed indicating both the minimum and maximum temperature limits. It was found that two dyes—for example, a red and blue forming a violet—can be dissolved in absolute alcohol without combining chemically. When such a solution with the right proportions of the components is applied to the part to be heated, the lower temperature dye will disappear at its own particular temperature and time interval, thus changing sharply the violet mixture to either a red or blue, depending on which is the lower component dye. In other words, the higher component dye is left on the material. If the time interval and temperature are then increased to a point corresponding to the higher component dye, it will also disappear. This "double indicator" in a single solution, then, will enable one to tell by inspection whether the heat applied was below, within the limits set, or above the maximum limit.

The following dyes when mixed in right proportions will act as good double indicators: (*a*) Chemco blue-Chemco red, (*b*) C. P. 196–malachite green, (*c*) malachite green–rubine red, (*d*) erythrosin–neptune blue.

Applications

(1) In many heating processes where a definite amount of heat must be applied during a certain time interval, the use of a dye as a heat indicator will be found efficient. To determine whether the heat applied was within the proper limits, the disappearance or change of color is noted.

(2) A very important use, and one to which a dye is admirably adapted, is that of determining the heat distribution of any material to which it is applied. The heat distribution is noted by the distribution of the remaining color or the order in which the color disappears.

(3) For glass annealing a suitable dye is applied to the part to be measured, or on a test plate which is subjected to the same heat conditions. The dye chosen is one that will just disappear or change to another color.

(4) In baking cements or mixtures which require a definite amount of heat, the proper indicator may be mixed in the compound, the amount used being determined by tests. The disappearance of the color in the compound will indicate that sufficient heat has been supplied.

(5) Still another use of dyes is an indicator of overheating which any electrical instrument or part may receive. An inspection of the part coated with the proper dye will immediately indicate whether it has been overheated by the presence or absence of the color.

A Modified Test for Phthalates

With Particular Reference to the Detection of Diethylphthalate[1]

By R. E. Andrew

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The use of diethylphthalate as a denaturant for industrial alcohol to be used in the manufacture of toilet preparations has brought about the necessity of reliable tests for its detection, either in the manufactured preparations or in products which may have been illegally derived therefrom.

Several tests have been described[2] in which heating with resorcin is recommended, the final results being the development of green or yellow-green fluorescence if the test is positive.

In the author's experience the criticism of all these tests is that satisfactory blanks cannot be obtained; the reagents alone may develop fluorescence of such a color and intensity as to make conclusions with regard to an unknown sample doubtful. In a series of trials in which reduced periods of heating the acid-resorcin mixture were tried, it appeared that the difficulty arose at this stage in the process. It was found that no heat other than that developed on neutralizing the alkaline mixture with sulfuric acid was necessary or advisable. The modified test is as follows:

Method

To 10 cc. of the solution to be tested in a small porcelain capsule add 5 drops of a 10 per cent sodium hydroxide solution. Evaporate over a steam bath to dryness and then add 0.5 cc. of a 5 per cent resorcin solution and again evaporate to dryness. Remove from the steam bath and at once add 6 drops of concentrated sulfuric acid and mix thoroughly by rotating the capsule. When cool add 10 cc. of water and transfer to a test tube, rinsing the capsule with 10 cc. of water. Add 5 cc. of a 10 per cent sodium hydroxide solution. A green fluorescence will at once appear if the test is positive, the color of the fluorescence varying from green to yellow-green, according to the amount of phthalate present.

Alcohol of known purity gave a negative test—i. e., no fluorescence. Ten cubic centimeters of pure alcohol to which had been added 0.1 cc. of a 1 : 500 solution of diethylphthalate (0.0002 gram) gave an unmistakable fluorescence. Positive tests were also obtained when small amounts—i. e., 0.0010 to 0.0020 gram—of this denaturant were added to gin and whiskey, the procedure as outlined being applied directly to these substances without previous distillation. In the presence of considerable amounts of extractive material it was found best to (1) extract the diethylphthalate with petroleum ether, evaporate the solvent at room temperature, take up the residue with alcohol and apply the test, (2) distil rapidly and apply the test to the distillate.

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[1] Received February 27, 1923. Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Mulliken, "Detection of Pure Organic Compounds," Vol. I, p. 107; Allen, "Commercial Organic Analyses," Vol. III, p. 546; Lyons, *J. Am. Pharm. Assoc.*, **11** (1922), 262; Handy and Hoyt, *Ibid.*, **11** (1922), 928.

The Gelatin-Tannin Reaction[1]

By Arthur W. Thomas and Alexander Frieden

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Gelatin is completely precipitated by gallotannic acid when the ratio of tannin to gelatin is not less than 2 : 1 and the gelatin-tannin precipitate is not soluble in excess of tannic acid.

There is a definite hydrogen-ion concentration for each sort of vegetable tannin for best precipitation. If the solution is not adjusted to or near this C_{H^+}, the precipitate may fail to form.

The presence of a neutral electrolyte broadens the C_{H^+} range for precipitation.

At the optimum C_{H^+} tannin can be detected in dilutions as high as 1 part tannin in 100,000 to 200,000 parts of water, depending upon the source of the tannin.

Aging of gelatin solutions has no effect on the sensitivity in testing for tannin provided bacterial action is prevented.

QUANTITATIVE data on the mutual precipitation of gelatin and tannin are of timely value in the proper manipulation of the gelatin test for tannin, so important in the leather industry, of the tannin test for proteins, of interest to the biochemists, and also to aid in the elucidation of the question concerning the nature of the combination between these substances of great chemical complexity.

PREVIOUS WORK

Seguin[1,*] is credited with the discovery of the precipitation of gelatin by those vegetable extractives which have the power of tanning skin, although Seymour-Jones[2] claims that in 1762 Lewis found that galls contained an astringent substance which would precipitate gelatin from solution. Proust[3] attempted to show that the gelatin-precipitating property was identical with the ability to tan skins, and a year later Humphrey Davy[4] pointed out that (1) different vegetable tannins required different amounts of gelatin for saturation, (2) the composition of the coagulum, which in the average was 100 gelatin to 82.5 tannic acid, depended upon the concentrations of gelatin and tannin used, and (3) the coagulum was soluble in an excess of gelatin.

Following Davy, a number of investigators,[5] all criticizing each other, suggested composition ratios of the coagulum varying from 59 to 136 parts of tannin acid to 100 parts of gelatin.

Graeger[6] suggested the quantitative use of the reaction for determination of the purity and amount of gelatin in a given solution, and Fehling[7] devised a method whereby tannin could be determined by titration with a gelatin solution. These quantitative methods were based, of course, upon an accepted combining ratio which pleased the inventor of the method, but which unfortunately never agreed with that found by others.

The importance of the presence of electrolyte for sharp coagulation was first noted by Risler-Beurat,[8] who recommended the addition of alum, and this innovation was demonstrated by Schneider[9] to be an improvement in the quantitative determination of tannin. Later, Schultz[10] recommended saturation with ammonium chloride, finding this salt more efficient than either sodium sulfate, acetate, or borate.

Later workers offered evidence for and against the quantitative value of the tannin-gelatin reaction.[11] Lowenthal's[12] method, based on the titration of excess tannin by permanganate in the filtrate after mutual gelatin-tannin precipitation in the presence of sodium chloride and hydrochloric or sulfuric acid, won the approval of Procter[13] and Katheriner,[14] although later Simand[15] claimed the addition of acid to be a source of error, since "gelatin tannate" was dissolved thereby. Jean[16] proposed the addition of sodium bicarbonate and sodium chloride, while Dreaper and Wilson[17] demonstrated that the amount of acid or alkali is of deep significance, since an excess of either results in dissolution of the coagulum or prevention of formation of any precipitate whatsoever. Wood[18] showed that borax and ammonium oxalate inhibited the reaction and that the lower the ash content of the gelatin, the less tannin is precipitated by it, which merely means that a certain amount and kind of neutral electrolyte is essential for best results.

Trunkel[19] found that while the coagulum is peptized by an excess of gelatin, excess of tannin has no effect, and that under conditions of complete mutual precipitation, the coagulum is absolutely insoluble in water, although completely soluble in alcohol provided it is treated with alcohol before it has had a chance to dry! He also demonstrated that the combining capacity of gelatin is a function of its purity and claimed that aged gelatin solutions were not so efficient as freshly prepared ones.

Perusal of this mass of experimental contradictions shows that one or more controlling conditions were not known by the earlier workers. One condition that was not controlled and which may account for the wide discrepancies is the hydrogen-ion concentration, which has been demonstrated by modern research to be of paramount importance in any reaction in which protein plays a role. The first to take this into consideration were Michaelis and Davidsohn,[20] to whom we shall refer later.

PURPOSE OF PRESENT WORK

The purpose of this investigation is to show the best ratio of tannin to gelatin and the optimum hydrogen-ion concentration for the mutual precipitation of gelatin and tannin, and to demonstrate the delicacy of the test, under proper conditions, for tannin in solutions of various important vegetable tanning materials.

MAXIMUM MUTUAL PRECIPITATION

Gallotannic acid containing 11.6 per cent water and 0.07 per cent ash and gelatin containing 16.6 per cent water and 1.16 per cent ash were used, except for the experiments recorded in Tables I and II, where an edible gelatin was used.

TABLE I

Ratio of Tannin to Gelatin	Volume of Precipitate Cc.	Appearance of Supernatant Liquid	Test of Supernatant Liquid for Gelatin	Tannin
20	0.4	Clear, yellow	–	+
10	0.9	Clear, yellow	–	+
8	0.9	Clear, yellow	–	+
6	1.4	Clear, slight yellow	–	+
4	1.5	Clear, slight yellow	–	+
2	2.5	Clear, colorless	–	Almost –
1	1.8	Milky	+	..

The method used for determining the maximum mutual precipitation of gelatin and tannin was as follows: The required amount of tannin solution was allowed to run into a 100-cc. graduated tube with a long, tapering end graduated to 0.01 cc. (oil tube). The gelatin solution was then added, and the mixture shaken and centrifuged for 30 minutes at a force of 1000 "times gravity."

The volume of the precipitate at the bottom of the tube gave an indication of the maximum precipitation, though it is to be noted that the comparison of the volumes of precipitate was not always extremely exact, owing to imperfect packing. The appearance of the supernatant solution in the tube and the presence or absence of gelatin and tannin therein were additional aids in determining the maximum mutual precipitation.

The solutions used in these experiments were made up so that the total reacting mixture contained 1 gram in 100 cc.

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[1] Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. Contribution No. 413 from the Chemical Laboratories, Columbia University.

[*] Numbers in the text refer to the bibliography at the end of the article.

of solution. The proportions of gelatin and tannin were varied, at the same time varying the hydrogen-ion concentration in order to get the approximate limits for the optimum.

The results obtained at a reaction of $C_{H^+} = 10^{-4.0}$ are shown in Table I.†

The ratios noted above were tried at $C_{H^+} = 10^{-2}$, 10^{-4} and 10^{-8}. At $-\log C_{H^+} = 2$, dense turbidities formed at all ratios, but did not settle out even upon centrifuging. At $-\log C_{H^+} = 6$, slight turbidities were obtained, whereas at $-\log C_{H^+} = 8$, no effect was obtained, the solutions remaining clear.

These results show that the best ratio of gelatin and tannin is 1:2, and unless otherwise stated this ratio was adhered to in subsequent experiments.

Solutions were prepared at various C_{H^+}'s between $10^{-2.5}$ and $10^{-5.5}$, where the total concentration of gelatin and tannin was 1, 0.1, and 0.02 per cent, all of which showed that the optimum reaction lay between the limits of $-\log C_{H^+} = 4$ to 5.

The more exact determination of the optimum reaction, where the total concentration of gelatin and tannin was 0.1 per cent, is shown in Table II.

TABLE II

$-\log C_{H^+}$	Appearance of Supernatant Solution	Volume of Precipitate Cc.
3.9	Opalescent	0
4.1	Opalescent	0.20
4.2	Clear	0.35
4.3	Clear	0.35
4.4	Clear	0.40
4.5	Opalescent	0.25
4.6	Opalescent	0
4.7	Milky	0
4.9	Opalescence	0
5.1	Slight opalescence	0

All these supernatant solutions gave precipitates on addition of gelatin to the supernatant solution, the minimum, however, being obtained with the solution at $C_{H^+} = 10^{-4.4}$.

From these results, it is concluded that the optimum C_{H^+} for the mutual precipitation of gelatin and gallotannic acid is $10^{-4.4}$. A 1 per cent solution of tannin was treated with a 0.1 per cent solution of gelatin at various C_{H^+}'s, as in Table II. The results obtained show that the optimum C_{H^+} remains about the same.

TABLE III

$-\log C_{H^+}$	Appearance of Supernatant Solution	Volume of Precipitate Cc.
3.9	Clear, yellowish	0.90
4.1	Clear, yellowish	1.10
4.3	Clear, yellowish	1.15
4.5	Clear, yellowish	1.20
4.7	Cloudy	0.90
4.9	Milky	0.80
5.1	Opalescent	0
5.3	Slightly opalescent	0

Michaelis and Davidsohn[20] report the optimum reaction to vary between $C_{H^+} = 10^{-3.8}$ and $10^{-5.7}$ depending upon the ratios of tannin to gelatin and the masses of the same in the solution. One reason for the discrepancy between their findings and those of the authors is the fact that in a number of the very meager experiments made by them there was an excess of gelatin.

In anticipation of a possible criticism of the restriction of the data to one given sample of gelatin, it was deemed advisable to try other specimens of gelatin. In Tables I and II an edible gelatin of unknown history was used. Duplicating the mutual precipitations over a range of C_{H^+} of $10^{-3.0}$ to $10^{-5.5}$, using two different brands of gelatin, showed about the same results at each C_{H^+}, except that the greatest precipitation of tannin occurred at $C_{H^+} = 10^{-4.4}$ for the first gelatin, while at $C_{H^+} = 10^{-4.6}$ for the second specimen.

These figures show a slight difference in the optimum point for the three gelatins.

EFFECT OF SALT

Since 1860 it has been known that the precipitation of tannin by gelatin is made more complete by the addition of an electrolyte. In the official method for testing for tannin used by the American Leather Chemists Association, the gelatin solution is made up to contain 10 per cent of sodium chloride. It was desirable, therefore, to study the effects of electrolyte on the mutual precipitation of gelatin and tannin.

Preliminary experiments have shown that the addition of sodium or potassium chloride widens the range of C_{H^+} for precipitation, and that these electrolytes will cause further precipitation only at $-\log C_{H^+}$ below 4 or above 5. Between 4 and 5 the salt apparently exerts no influence.

Tannin and gelatin solutions with final concentration 0.1 per cent and tannin-gelatin ratio 2:1 were mixed in the usual way at various C_{H^+} values. The solutions were (1) centrifuged for 30 minutes and (2) sodium chloride was added to make the final concentration of the solution 0.01 *M*. The solutions were again centrifuged and (3) more sodium chloride was added to make the final concentration 0.1 *M*. The results obtained are given in Table IV.

TABLE IV—EFFECT OF SALT

$-\log C_{H^+}$		(1) No NaCl	(2) 0.01 NaCl	(3) 0.1 NaCl
3.0	No ppt.	Faint opalescence	Milky	Increased turbidity
3.5	No. ppt.	Slight opalescence	Opalescent	....
4.0	Ppt.	Slight opalescence	Clear	No further effect
4.5	Ppt.	Slight opalescence	Clear	No further effect
5.0	No ppt.	Slight opalescence	Turbid	Clear
5.5	No ppt.	Clear	Opalescent	....

Solutions were made in sodium chloride so that the final concentration of salt was in one case 0.01 *M* and in another 0.1 *M*. Higher concentrations did not seem to affect the mutual precipitation, but rather to salt out the tannin from the tannin solution. This salting-out effect was very marked with concentration of 1 *M* and upward.

Table V gives the results obtained with 0.01 *M* sodium chloride solution, and Table VI, when a 0.1 *M* solution was used.

TABLE V

$-\log C_{H^+}$	Effect		Effect of Additional NaCl
1	Milky	No ppt.	None apparent
2	Opalescent	No ppt.	Milky
3	Opalescent	No ppt.	Ppt.
4	Ppt.	....	None apparent
5	Opalescent	No ppt.	Ppt.
6	Clear	No ppt.	Slight ppt.
7	Clear	No ppt.	Opalescence
8	Clear	No ppt.	None

TABLE VI

$-\log C_{H^+}$	Effect		Effect of Additional NaCl	Test for Gelatin
1	Very slight ppt.	Clear soln.	None	Negative
2	Slight ppt.	Clear soln.	None	Negative
3	Ppt.	Clear soln.	None	Negative
4	Ppt.	Clear soln.	None	Negative
5	Ppt.	Clear soln.	None	±
6	Very slight ppt.	Milky	Ppt.	Positive
7	No ppt.	Opalescent	Ppt.	Positive
8	No ppt.	Clear	Ppt.	....

It is thus seen that the effect of electrolyte is only to widen the range of C_{H^+} for precipitation.‡ However, while widening the range, it does not produce maximum precipitation, nor does it have an effect on the mutual precipitation at or near the optimum C_{H^+}.

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† All hydrogen-ion concentrations reported in this paper were determined electrometrically. Solutions were adjusted to the hydrogen-ion concentrations throughout by means of sodium hydroxide or hydrochloric acid, except for the data recorded in Tables VIII and IX where phosphate buffers were used for the dilutions up to $C_{H^+} = 10^{-4}$.

‡ In accordance with Weiske, *Z. physiol. Chem.*, **7**, 460 (1882), who found that gelatin and tannin would not precipitate each other from all solutions, while the addition of a neutral salt to such solutions effected a positive result.

APPLICATION TO VEGETABLE TANNING EXTRACTS

No data are available concerning the limits of detection of tannin by the "gelatin-salt" test. In order to establish the delicacy of the test with several important tanning materials, it was required first to determine the optimum hydrogen-ion concentration for each extract. While this was found to be at $C_{H^+} = 10^{-4.4}$ to $10^{-4.6}$ for gallotannic acid, it is not necessarily true for all tannins, as the figures in Table VII show.

TABLE VII—OPTIMUM C_{H^+} RANGE FOR TANNIN-GELATIN PRECIPITATION

EXTRACT	$-\text{Log } C_{H^+}$
Larch	4.0 to 3.5[a]
Oak	3.5 to 4.0
Hemlock	4.0 to 4.5
Quebracho	4.0 to 4.5
Wattle	4.5 to 4.0
Gambier	3.5 to 4.0

[a] The optimum reaction is given last in each case.

The optimum for gallotannic acid-gelatin precipitation suggested that the combination took place at or very close to the isoelectric point of gelatin ($C_{H^+} = 10^{-4.6}$ to $10^{-4.7}$), but the data offered above indicate that the hydrogen-ion concentration is of significance to the components of the tanning extract as well as to the gelatin.

The delicacy of the test for tannin at the optimum C_{H^+} for each material is given below (Table VIII). The gelatin solution consisted of 1 gram gelatin and 10 grams sodium chloride, made up to 100 cc. in distilled water. Two drops of this solution were let fall into 10 cc. of the tannin solution to be tested. Since so little gelatin is used it is unnecessary to adjust the gelatin to the optimum C_{H^+}. To demonstrate the necessity of adjusting the tannin solutions to optimum C_{H^+}, the limits of delicacy are also given for the cases where the tannin solutions were diluted with distilled water just as they were without paying any attention to the acidity.

TABLE VIII

EXTRACT	Limit of Detection at Optimum C_{H^+} 1 Part in	Parts Tannin in Parts Water in Distilled Water 1 Part in
Larch	150,000	20,000
Oak	150,000	7500
Hemlock	130,000	6500
Quebracho	130,000	17,000
Wattle	200,000	20,000
Gambier	110,000	30,000

It is evident that when extreme delicacy is required, the reaction of the tannin solution must be adjusted, since, as shown above, there is a marked falling off in limits of detection when an extract is diluted with distilled water without regard to the C_{H^+}. In this connection it is interesting to note that Wilson and Kern[21] reported the delicacy of the "gelatin-salt test" (dilution at which test was negative) as follows: quebracho, 1: 11,300; hemlock bark, 1: 5600; oak bark, 1: 5700; larch bark, 1: 6300; and gambier, 1: 6500. In their experiments the extracts, as found, were diluted with distilled water.

Owing to the confliction in the definition of tannin, it should be emphasized that all the figures in this paper are based on the Wilson and Kern[21,22] method, which defines tannin as those substances which irreversibly combine with hide substance.

The extracts were then made up at $-\log C_{H^+} = 6, 7, 8, 9$, and 10, and the limits of detection of tannin were determined with results as tabulated below. In each case the gelatin solution was adjusted to the same C_{H^+} as the tannin solution.

The abrupt change in delicacy between $C_{H^+} = 10^{-6}$ and 10^{-7} is due to a difference in determination of end point. At 10^{-6} the limit of detection was based upon appearance of a turbidity, but due to the darkening of the solutions at higher alkalinities such end point became impossible to detect and it was necessary to look for the appearance of a definite coagulum. At $C_{H^+} = 10^{-10}$, precipitation was found to take place—at higher concentrations of tannin than at 10^{-9}, to be sure—but the values were too indefinite to be reported, on account of the very dark color of the solutions.

TABLE IX

	Limits of Detection			
	1 Part Tannin in Parts Water			
$-\text{Log } C_{H^+}$	6	7	8	9
Wattle	30,000	8000	4000	1500
Quebracho	30,000	20,000	7500	2500
Larch	15,000	1750	1000	500
Hemlock	10,000	4800	2400	1500
Gambier	10,000	1000	750	400
Oak	7000	1750	750	500

The figures strikingly demonstrate the significance of hydrogen-ion concentration in the gelatin-tannin reaction. Tests on the acid side of the optimum were not performed because the tannin particles are precipitated in acid solutions.

It is to be emphasized that the delicacies tabulated above are extreme figures representing the faintest turbidities and precipitates visible upon careful scrutiny only by one very familiar with the technic. In practical and hurried use the delicacies noted above would not be obtained.

In testing spent tan liquors it would be necessary, owing to the color of such liquors, to set up a blank for comparison with the tube to which the gelatin-salt reagent is added.

Since the standard gelatin-salt reagent is readily putrescible and its efficiency thereby rapidly declines, it is necessary to prepare it fresh daily. A series of gelatin solutions was prepared and allowed to stand at room temperature to see whether this troublesome feature could be eliminated. Four mixtures were prepared, all 1 per cent gelatin, as follows: (*a*) in distilled water at $-\log C_{H^+} = 7$, plus 1 per cent sodium fluoride, (*b*) same as (*a*) except use of toluene instead of sodium fluoride, (*c*) in distilled water adjusted to $-\log C_{H^+} = 4.6$ plus 1 per cent sodium fluoride, and (*d*) same as (*c*) except that toluene was used instead of sodium fluoride.

The oldest solutions, prepared on June 24 and tested on November 25, all proved to be as efficient as a freshly prepared gelatin-salt reagent. The reaction of $-\log C_{H^+} = 4.6$ as well as 7 was selected, because gelatin is readily putrescible at $C_{H^+} = 10^{-7}$, while it is exceedingly resistant to bacteria at 4.6, not entirely because of its isoelectric condition at the latter, but also because the activity of liquefying bacteria is apparently inhibited or prevented at $C_{H^+} = 10^{-4.4}$.

It is therefore unnecessary to prepare the gelatin-salt reagent fresh daily, since it has been shown that such solutions kept for five months at least, provided a suitable preservative such as toluene or sodium fluoride is present, are just as efficient as freshly prepared solutions.

ACKNOWLEDGMENT

The authors are indebted to A. F. Gallun & Sons Co., of Milwaukee, Wis., for grants in aid of this investigation.

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The Measurement of Temperature in Rubber and Insulating Materials by Means of Thermocouples[1]

By Ellwood B. Spear and J. F. Purdy

The Goodyear Tire and Rubber Co., Akron, Ohio

The thermocouple methods hitherto employed are shown to give temperature measurements in rubber articles, tires, etc., which are much too low, unless there is little or no temperature differential for several inches along the wires from the thermal junction.

Curves are given whereby many temperature measurements recorded in the literature may be corrected.

A new thermocouple casing is described which has been found convenient for the measurement of temperatures in solid or pneumatic tires while the latter are in use on the road.

Two methods have presented themselves to various investigators as possible ways of measuring the operating temperatures of pneumatic tires. One is the determination of the temperature from pressure-volume changes of the air confined in the inner tube. The other method involves the use of thermocouples.

Considerable attention has been paid to the first-mentioned method.[2] In order that reliable results may be obtained it is necessary to measure very accurately changes of pressure, the expansion of the tire, and leakage of air from the inner tube during the time the tire was rolling. Considerable calculation is necessary to derive the temperature from the data obtainable. The method is best suited to laboratory tests. The greatest objection to this method lies in the fact that only the average temperature in the tube is measured. This is not the temperature of the carcass of the tire. Recent tests have shown that the carcass of a truck tire may run 60° F. above the temperature of the air inside the tube. In many cases it may indicate that one tire is hotter than another, but this is not invariably reliable, especially when testing tires of radically different construction. It does not indicate which portion of the tire is the hottest. Some means are necessary whereby the carcass of a tire can be explored, and its actual temperature and its hottest portions known.

To fill this need the thermocouple has been brought into use. At first thermocouples were placed between the plies of the tires when building. Very meager results were obtained by this method, for as soon as the tire began to roll the wires were broken by the flexing action.

More recently means have been employed to insert a thermocouple into the tire from the outside to some point whose temperature was to be measured. The thermocouples were made of No. 28 gage, copper-constantan wire twisted together and soldered. One way of inserting the thermocouple in the rubber was to pass the couple through an eye in the head of an awl.[3] The awl was thrust into the rubber, carrying the couple with it. On withdrawing the awl the couple remained inbedded in the rubber. When tire temperatures were measured the thermocouple was inserted to a depth of from $^1/_4$ to $1^1/_4$ inches.

Experiments in this laboratory have shown that thermocouples used in the manner described above give temperature readings which are far too low. The error depends upon the size wires used, the depth to which they are inserted, the temperature differential along the wire, and the thermal conductivity of the rubber stock whose temperature is being measured. The correction to be applied must be determined for the particular conditions under which the thermocouple is used.

The cause of the erroneous readings obtained by the foregoing method is explained as follows: The thermocouple wires are very good conductors of heat, while rubber conducts heat poorly. When thermocouple wires are imbedded only a short distance in the rubber, as is necessarily the case in a tire, only a small surface of wire is in contact with the rubber. Heat from a thin film of rubber immediately surrounding the wires is rapidly conducted away by the wires. Heat from the surrounding mass of rubber is not transferred to the wires so rapidly as heat is conducted away by them. As a result the temperature of the thermocouple and the thin film of rubber around it is kept lower than that of the surrounding mass of rubber.

Experiments in this laboratory have shown that when using No. 28 gage wire to measure the temperature of rubber at least $3^1/_2$ inches of the wire must be kept at the same temperature as the rubber at the point where the temperature is to be measured, in order to secure correct readings. That is to say, there must be no temperature differential along the wires for at least $3^1/_2$ inches from the couple. When this length of wire is in contact with the rubber, enough surface is exposed to the rubber to allow sufficient heat to be transferred to the wires to maintain the thermocouple at the temperature of the surrounding mass of rubber. In cases of temperatures higher than those ordinarily measured in rubber compounds, or in cases of other articles of lower heat conductivity, it will probably be necessary to insert the thermocouple deeper in order to insure correct temperature readings. No experimental work has been carried out in this regard on substances other than rubber.

DEPTH OF INSERTION OF THERMOCOUPLE NECESSARY

The apparatus used to show the proper depth of insertion of a thermocouple necessary to give correct readings is shown in Fig. 1.

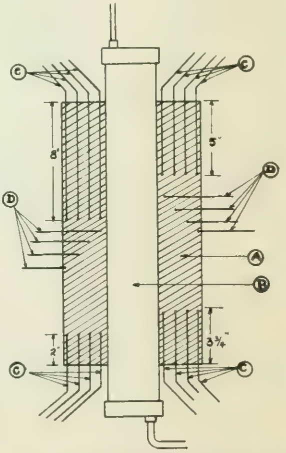

Fig 1—Apparatus to Determine Error in Readings of Thermocouples Inserted to Various Depths in Rubber

A—Rubber cylinder built around a steam pipe; half of cylinder removed to show position of thermocouples

B—Steam pipe through which live steam was passed to heat the rubber

C—Thermocouples parallel to pipe imbedded to various depths in rubber

D—Thermocouples perpendicular to pipe imbedded to various depths in rubber

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[1] Presented before the Division of Rubber Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Ellenwood, *J. Soc. Automotive Eng.*, **10** (1922).

[3] "A Method of Measuring the Temperature at Different Points in the Body of an Automobile Tire." Research Bulletin, New Jersey Zinc Company, November, 1921.

A cylinder of rubber, *A*, made of a pure gum-sulfur mix (Fig. 1) was built around a $3^7/_{16}$-inch iron pipe, *B*. After the rubber cylinder was properly cured it was cut in half axially. Thermocouples, *C*, were placed between the halves. Each thermocouple was placed at a carefully measured distance from the pipe. The wires leading from the thermocouples were laid exactly parallel to the pipe. By placing the wires in this manner, the entire length of the wire imbedded in the rubber was surrounded by a mass of rubber at the same temperature as that surrounding the thermocouple. Sets of wires were imbedded in the rubber to various depths from 2 to 8 inches. The halves of the cylinder were than cemented together and cured for a short time in order to set the cement. Steam at any desired pressure could be passed through the iron pipe to raise the temperature of the rubber to the desired degree.

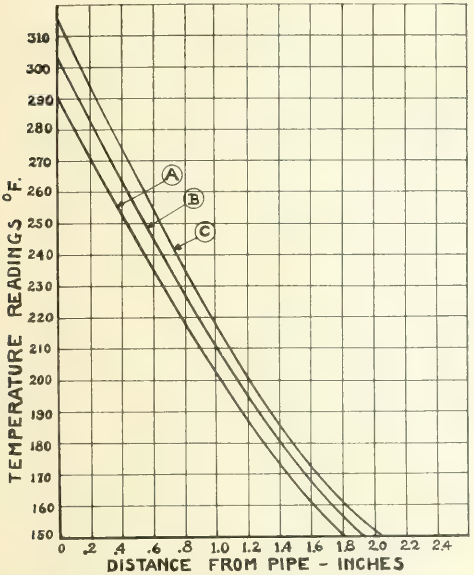

FIG. 2 READINGS OF THERMOCOUPLES IMBEDDED IN RUBBER TO VARIOUS DEPTHS

A Temperature readings of couples inserted 1 inch in rubber

B Temperature readings of couples inserted 2 inches in rubber

C—Temperature readings of couples inserted $3^3/_4$, 5, and 8 inches in rubber

Curve C represents the actual temperature

By this method it was found that the thermocouples of No. 28 gage wire imbedded $3^1/_2$ inches or more in the rubber gave the same temperature readings at any given distance from the steam pipe. Those imbedded less than $3^1/_2$ inches gave readings lower than the actual temperature at the point measured. Fig. 2 shows curves drawn from original data. The curves show the temperature readings of thermocouples imbedded to depths of 1 and 2 inches in the rubber and the actual temperatures as obtained by couples imbedded $3^1/_2$, 5, and 8 inches. Had the rubber not had such a low thermal conductivity, less than $3^1/_2$ inches insertion would doubtless have sufficed. In the experiment the temperature ranged as high as 300° F., thus covering any temperature usually found in rubber compounds.

Thermocouples inserted, as shown by *D*, Fig. 1, to depths of 2 inches and less, and having a greater temperature differential along the wires than was the case with couples *C*, Fig. 1, gave readings much lower than the actual temperature.

CORRECTION CURVES

In order to determine the corrections that must be made on thermocouple readings under conditions usually found when measuring tire temperatures, the apparatus shown in Fig. 3 was constructed. A thin slab of rubber, *B*, was laid over an electric hot plate, *A*. Other slabs of rubber, *C*, of any desired thickness could be laid on top of *B*. The actual temperature between the slabs *B* and *C* was measured by thermocouples having at least 6 inches of wire at the same temperature as the rubber about the couple. Previous experiments, as described above, had shown that such thermocouples would give correct temperature readings. Other thermocouples were inserted in the rubber and their readings compared with the actual temperature.

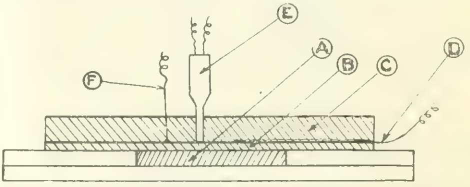

FIG. 3 APPARATUS TO DETERMINE ERROR IN THERMOCOUPLE READINGS

A—Electric hot plate

B—Thin slab of rubber

C—Slab of rubber of any desired thickness, through which thermocouples were inserted to slab *B*

D—Thermocouples placed to give actual temperature between slabs *B* and *C*

E—Tire thermocouple inserted in rubber

F—Thermocouples inserted in rubber with an awl, as is sometimes done in measuring tire temperatures

In this apparatus the thermocouples could be placed much more accurately in any desired position than was possible when using the rubber cylinder (Fig. 1). It also had the advantage of giving a much wider temperature range.

Thermocouples, *F*, Fig. 3, were inserted through slab *C* by means of an awl. The slab *C* was then laid in position so that the thermocouples *F* lay between slabs *B* and *C*. Thermocouples were made of insulated copper-constantan wires twisted together at the ends and soldered. The temperature gradient through the slab of rubber *C* represented very closely the temperature gradient in the carcass of a tire. Calibrations were made using two different rubber compounds. Both compounds are used in tires. One had a comparatively

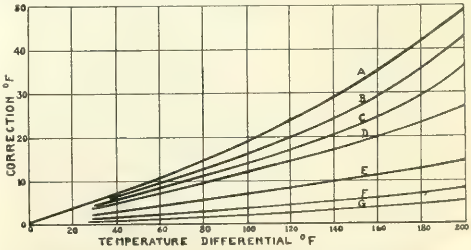

FIG. 4 CORRECTION TO ORDINARY THERMOCOUPLES INSERTED TO VARIOUS DEPTHS IN RUBBER OF VERY LOW THERMAL CONDUCTIVITY

A No. 28 gage wire inserted 0.30 inch in rubber

B—No. 28 gage wire inserted 0.55 inch in rubber

C—No. 28 gage wire inserted 0.85 inch in rubber

D—No. 28 gage wire inserted 1.15 inches in rubber

E—No. 36 gage wire inserted 0.30 inch in rubber

F No. 36 gage wire inserted 0.55 inch in rubber

G No. 36 gage wire inserted 0.85 inch in rubber

Temperature differential is equal to the potentiometer reading minus the temperature of the air immediately around the rubber low thermal conductivity, the other had a comparatively high conductivity. Figs. 4 and 5 show the corrections to be applied to thermocouples of No. 28 and 36 gage when inserted as shown by *F*, Fig. 3.

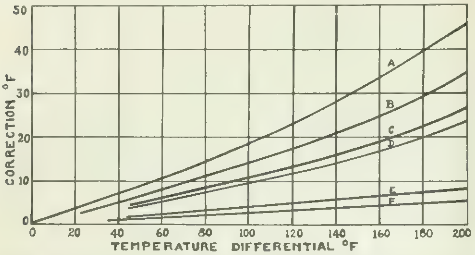

Fig 5—Correction to Ordinary Thermocouples Inserted to Various Depths in Rubber Stock of Medium Thermal Conductivity

A—No. 28 gage wire inserted 0 30 inch in rubber
B—No. 28 gage wire inserted 0.55 inch in rubber
C—No. 28 gage wire inserted 0.85 inch in rubber
D—No. 28 gage wire inserted 1.15 inches in rubber
E—No. 36 gage wire inserted 0.55 inch in rubber
F—No 36 gage wire inserted 1 15 inches in rubber

Temperature differential is equal to the potentiometer reading minus the temperature of the air immediately around the rubber

New Type of Thermocouple

Fig. 6 shows a thermocouple developed by the authors which has given very satisfactory results. A cylinder of hard maple is turned to the dimensions shown. A thermocouple is made of No. 36 or No. 40 gage copper and constantan wires twisted together and soldered, or fused as desired. A small copper disk $^3/_{16}$ inch in diameter and $^1/_{64}$ inch thick is soldered to the thermocouple. The disk is then sprung into a depression at the end of the tube. A maple plug is turned to fit tightly into the top of the tube. Two heavy terminals, one of copper and one of constantan, are fixed in the plug. The small thermocouple wires are attached to these terminals. Magnesium oxide is sifted lightly around the wires until the tube is filled. The plug is then glued into the top of the tube.

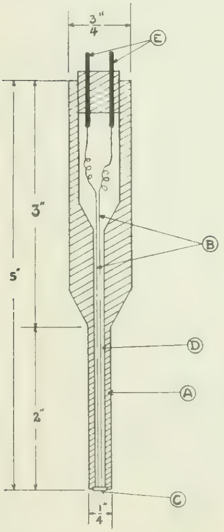

Fig. 6 Tire Thermocouple

A—Hard maple tube turned on lathe
B—No. 36 gage copper and constantan wires
C—Copper disk and thermocouple
D—Magnesium oxide packed loosely around wires
E—Copper-constantan terminals

This type of thermocouple is inserted into a hole drilled in the tread of a tire to some point in the carcass. By using a high-speed drill (1800 to 2400 r. p. m.) a clean hole can be made. The hole is just large enough to admit the thermocouple, thus excluding all air and allowing the copper disk, or heat collector, to press tightly against the bottom of the hole. By using wires of very small diameter the heat loss by conduction along the wires is greatly reduced. These fragile wires are completely protected by the maple tube. The copper disk soldered to the thermocouple acts as a heat collector. It exposes a comparatively large surface to the rubber, thus facilitating the transfer of heat from the rubber to the thermocouple. This compensates to a large degree for the lack of depth of insertion of the thermocouple in the rubber.

The purpose of the magnesium oxide in the tube is to aid in insulating the wires from heat from the sides of the hole. This will mask, if not wholly eliminate, the effect of the temperature gradient in the tire. For any given depth of insertion the temperature will depend only upon the actual temperature at the point being measured and the temperature of the air immediately surrounding the tire. This makes possible a study of the different temperatures found at various points in a tire carcass.

The thermocouples are easily reproducible, and give identical readings on calibrating.

The correction for this type of thermocouple is shown in Fig. 7. The depth of insertion of the thermocouple, the potentiometer reading, and the temperature of the air around the tire are easily found. When they are known the correction to be added to the thermocouple is found from the chart. This chart covers a much wider range of conditions than will ordinarily be found when measuring tire temperatures. Usually a correction of 6° or 8° F. is the largest that need be made. Because the errors in the readings of this type of thermocouple are small, the difference in the correction to be applied when stocks of different thermal conductivities are measured is so small as to be negligible.

In addition to the calibration made in the apparatus shown in Fig. 3, the tire thermocouple was also calibrated in a 40 x 8 inch tire. The tread and several plies were laid back. Thermocouples were made of No. 36 gage wires. These couples were placed between the plies in such a manner that at least 6 inches of the wires were kept at the same temperature as the thermocouple. The plies were then cemented down and given a short cure, exactly as is done when repairing a tire. The thermocouples between the plies gave the

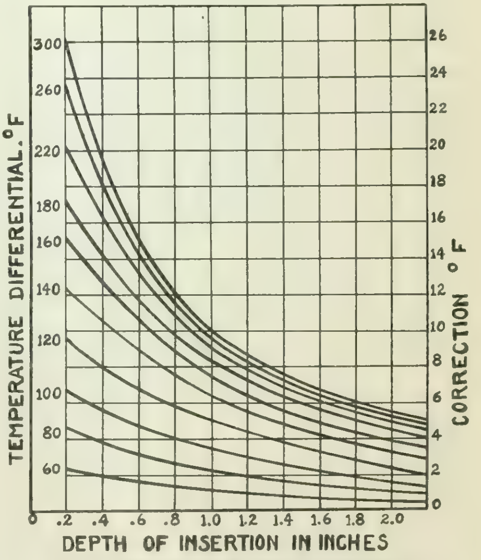

Fig 7 Correction Curves for Tire Thermocouples

Temperature differential equals the potentiometer reading minus the temperature of the air immediately around the tire actual temperatures. Holes were drilled through the tread of the tire to various depths to admit the tire thermocouple. The tire was heated by a sectional air bag through which steam could be passed at any desired pressure. The results of the calibration of the thermocouples in this manner checked with those previously obtained.

Drilling a hole in the tread of a tire to receive the thermocouple is not so severe on the tire as one might suppose. After a year's experience using this method in the laboratory, no tire has been found in which premature separation between the plies has occurred due to drilling the hole. In a tire having twelve plies of fabric, the writers have drilled through nine plies and still operated the tire for an extended time. When this method is used on road tests a rubber plug inserted in the hole will exclude all dirt. No rubber cement is necessary to keep the plug in place. When a reading is desired the plug can easily be removed with a pair of sharp-nose pliers.

Two precautions must be taken when using the tire thermocouple in order to secure correct temperature readings. The first is to allow the thermocouple to remain in position long enough to overcome the lag in the thermocouple. This takes about one minute, but varies slightly under different conditions of temperature. The other is the correction necessary for the time of reading after the tire stops. As soon as the tire stops rolling it begins to cool. Since the temperature cannot be taken instantly, it is always necessary to note the exact time of stop and the exact time when the temperature is taken. The rate of cooling of the tire should be observed and from the cooling curve a correction can be made for the drop in temperature between the time when the tire stops rolling and the time when temperature is taken.

Sodium Hypochlorite[1]

I—The Preparation of Concentrated Sodium Hypochlorite Solutions of Great Stability for Use in Food Factories, Milk Plants, Etc.

By **Harper F. Zoller**

The Nizer Laboratories Co., Detroit, Mich.

A demand for cheap sodium hypochlorite exists in the United States because of its rapidly increasing use as a disinfecting agent in food factories and elsewhere.

A method for making strong sodium hypochlorite solutions of 2 to 5 per cent available chlorine from sodium hydroxide, sodium carbonate, and drum chlorine is given, and cost data are presented.

The value of much buffer material in the holding of the pH around 10.5 for the region of maximum stability of concentrated sodium hypochlorite solutions is the principle of a successful method of preparing such solutions.

The yield of sodium hypochlorite calculated from the weight of chlorine used is about 100 per cent. This points to a different conception of the chlorinating reaction than that which has been prevalent.

METHODS for the preparation of sodium hypochlorite are so numerous that it seems almost unnecessary to add one more to the richly laden literature. But the methods heretofore advanced have been of value only to the textile manufacturer. A specific hypochlorite solution was made for a special factory operation under a given set of working conditions. No method has been devised for the wholesale production of a stable hypochlorite solution which would be suitable for transportation or storage for use in other industries. This study of hypochlorites was undertaken for the express purpose of determining the true nature of hypochlorites in solution, their stability and activity, and of producing a method for their preparation in large or small quantities for industrial plants.

Our conceptions of the constitution and the physical and chemical behavior of hypochlorite have very materially changed in the last few years. Recently, there have been a few attempts to regulate the stability and bleaching properties of chlorinated alkali solutions by studying their alkalinity in an empirical fashion. Among these investigations are the observations of Higgins[2] that alkalies stabilize sodium hypochlorite solutions and lower the velocity of bleaching, while neutral salts increase the bleaching rate and decrease the stability. Renewed interest in hypochlorites, especially the alkali hypochlorites, for bleaching purposes in the textile industry has been strongly manifested in England during the last decade. In the United States the pendulum seems to have swung in another direction; we have become deeply interested in hypochlorites as sterilizing agents and general disinfectants. Calcium hypochlorite, or chloride of lime, is much less used than formerly, principally because of the high lime carrying power and the sluggishness of its suspensions. Sodium hypochlorite is more effective, is simpler to handle, and will not leave a film of lime at any time through its use.

Many factories and plants engaged in the production of food products would use sodium hypochlorite as a sterilizing rinse for their equipment, provided large quantities of a uniformly stable quality could be made readily available. The present market price is prohibitive to a factory of any size.

A careful search into the merits of hypochlorites as sterilizing agents under conditions where organic matter was mainly absent, at once revealed their value, and a series of studies was undertaken to determine suitable methods of preparing the one logical hypochlorite (sodium) in large quantities. These studies led to a consideration of the practical stability of this substance under the conditions to which it would be subjected in food factories and elsewhere, as distinguished from the properties expected of it as a textile bleaching agent.

A method is here outlined which will enable the average factory to prepare its own effective disinfecting agent simply and cheaply. In subsequent papers the writer will take up the activity of sodium hypochlorite in the presence of organic matter and its relative bactericidal efficiency. The method described in this paper is based upon the hydrogen-ion control system of manufacture. The solution is heavily buffered in order that the reaction of the solution will not rapidly change to yield an unstable solution. A sodium hypochlorite solution containing 5 per cent available chlorine is here considered to be a concentrated solution. Solutions containing 10 and even 15 per cent available chlorine are readily prepared using the same principle, but they are unwieldy and impractical for general use.

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[1] Received December 18, 1922.

[2] *J. Soc. Chem. Ind.*, **27**, 185 (1911).

STABILITY OF SODIUM HYPOCHLORITE

The first successful attempts to prepare stable, dilute hypochlorite solutions for purposes other than bleaching were those of Dakin,[3] and Cullen and Austin.[4] These attempts matured in the introduction of a serviceable antiseptic solution for medicinal and similar uses. But, owing to difficulties co-existent with the transportation and application of the Carrel-Dakin solution, a series of chloramines was developed which has in a measure superseded the Dakin solution.

Cullen and Austin found that between pH 9 and 10, Dakin's solution is very stable. This solution of sodium hypochlorite approximates a 0.44 per cent solution of available chlorine, or a 0.45 per cent solution of sodium hypochlorite.

Many attempts by others to prepare more concentrated solutions of sodium hypochlorite at a supposedly similar range of hydrogen-ion concentration (pH 9 to 10) have met with failure, the reason being, in the writer's estimation, a poorly buffered solution at the concentration sought. It is absolutely essential that the solution be heavily buffered between these limits of pH if a high concentration of hypochlorite is desired.

The methods in general use for the preparation of sodium hypochlorite are:

(*a*) Double decomposition of calcium hypochlorite (chloride of lime) with sodium carbonate or sodium sulfate.

(*b*) Electrolysis of sodium chloride with the production of sodium hypochlorite and hydrogen.

(*c*) Direct chlorination of sodium carbonate with chlorine gas.

Wherever large quantities of sodium hypochlorite are demanded, the first process is undesirable because of the variable character of commercial chloride of lime, and because of the large mass of residual calcium carbonate sludge which must be disposed of. In the electrolytic method it would be necessary to employ buffers along with the sodium chloride if a strong solution of sodium hypochlorite were desired; otherwise, it would be extremely unstable and the tax on the electrodes and equipment enormous. The direct chlorination method is the most practical one for universal practice of producing strong sodium hypochlorite solutions. It is the most easily controlled and can be made rapidly on a commercial scale.

In adopting the direct chlorination method of manufacture, the first step was to provide a solution with sufficient buffer material to hold the hydrogen-ion concentration in the region of pH 10 to 10.5. On the assumption that the zone of reaction required for the stability of Dakin's solution was applicable to stronger solutions of sodium hypochlorite, several preparations of 2, 3, 3.5, 5, and 10 per cent available chlorine were made and studied in regard to their stability. The results of the study showed that for maximum stability these strong solutions required that powdered phenolphthalein spread on their surfaces should show a faint but distinctly red color, and further, that a 1 per cent alcoholic solution of thymolphthalein should show a flash of blue color. When such a solution is analyzed for titrable alkalinity, available chlorine, and total chlorides, and calculations of the true hydrogen-ion concentration are made therefrom according to the scheme suggested by Cullen,[4] one finds that the reaction is in the region of pH 10 to 10.6. This is a higher pH than is desired for Dakin's solution. The quality and quantities of buffer materials used for the purpose of furnishing the necessary reserve alkalinity follow later in the section devoted to the specifications for the hypochlorite preparation.

The following table is compiled from a great mass of trial runs made to determine the correct quantities of alkalies and pH for optimum stability:

TABLE I

60% Caustic Ash %	Anhydrous Soda Ash %	Available Chlorine %	Approximate pH, Calcd when Freshly Made	Pink to Phenolphthalein (Powdered)	Blue Flash Thymolphthalein, Alcoholic 1%	Available Chlorine after 10 Days %
5	5	3.15	8.5	No	No	1.72
5	5	3.03	9.0	No	No	2.10
5	5	4.22	7.8	No	No	0.70
5	7.5	3.20	8.8	No	No	2.04
5	2.5	2.53	9.8	Yes	No	2.28
5	2.5	2.30	10.2	Yes	Yes	2.29
5	2.5	2.20	10.8	Yes	Yes	2.20
5	5	2.50	9.8	Yes	No	2.45
2.5	2.5	2.00	9.0	No	No	1.20
2.5	2.5	1.65	9.8	Yes	Faint	1.58
2.5	2.5	1.50	10.4	Yes	Yes	1.51
7.5	5	4.05	9.4	Yes	No	3.40
7.5	5	3.50	10.5	Yes	Yes	3.48
7.5	2.5	3.30	10.2	Yes	Yes	3.30
7.5	2.5	3.20	10.6	Yes	Yes	3.20
12.5	2.5	6.50	9.8	Yes	No	6.29
12.5	2.5	6.00	10.2	Yes	Yes	6.00
10	2.5	5.00	9.5	Yes	No	4.80
10	2.5	4.50	10.0	Yes	Yes	4.51
10	5	5.00	10.0	Yes	Yes	4.96
5	0	2.05	(?)	No	No	0.12
5	0	1.50	(?)	Yes	Yes	1.10

While all the buffer materials were serviceable, sodium carbonate, because of its availability and cheapness, proved superior. As far as could be estimated, there was no appreciable anion influence on the stability of the concentrated solutions among the above buffers. The criterion of the stability seemed to be the intensity of the alkalinity, which is here characterized as the hydrogen-ion concentration.

TABLE II—SHOWING RELATIVE EFFECT OF BUFFER MATERIAL (ANIONS) ON THE STABILITY OF SODIUM HYPOCHLORITE

60% Caustic Ash %	Buffer	% Buffer on Moisture-Free Basis	Pink to Powdered Phenolphthalein	Blue Flash to 1% Thymolphthalein	Available Chlorine Fresh %	Available Chlorine 30 Days Later %
7.5	Na_2CO_3	2.5	Yes	Yes	3.25	3.25
7.5	Na_3PO_4	2.5	Yes	Yes	3.19	3.17
7.5	$Na_2B_4O_7$	2.5	Yes	(?)	3.20	3.21
7.5	Na_2SiO_3	2.5	Yes	Yes	3.22	3.22
7.5	$NaHCO_3$	2.5	No	No	3.25	2.80

The influence of daylight on the stability is only minor. The use of amber-colored bottles is unnecessary. In ordinary clear glass bottles the hypochlorite solutions keep for 5 or 6 months with less than 10 per cent loss in available chlorine.

It is not necessary either to cool the alkali solutions below 40° C. while chlorinating them, or to store the resulting hypochlorite in a cold place. Whereas it is true that the activity of the hypochlorite solutions (chlorinating power) is accelerated by small increases in temperature, their internal decomposition is not noticeably accelerated at the stable region in pH 10 to 10.5.

QUANTITATIVE ASPECTS OF THE CHLORINE-GAS METHOD

When chlorine gas is passed into a mixed solution of sodium hydroxide and sodium carbonate, containing about 10 and 2.5 per cent, respectively, and the gas is stopped when the solution registers 5 per cent of available chlorine, it is found that the yield is 99 to 100 per cent. A temperature change from 15° to 40° C. does not affect this yield. There is no formation of either chlorate of perchlorate under these conditions, or, if there is a chance formation of one or both, they must revert immediately to the hypochlorite, since the chlorine is found in the available condition in the solution. As a matter of fact, when the sodium hypochlorite solution is titrated for the available chlorine concentration, with sodium thiosulfate and sodium iodide in acid solution, actually two equivalents are titrated for every mol (70.9 grams) of chlorine gas passed into the alkaline solution. It matters not whether these equivalents come from the bound oxygen or bound chlorine in the hypochlorite molecule, so long as experience shows that the complete activity of the hypochlorite solution is *not destroyed before it registers zero available chlorine.*

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[3] Dakin, *Brit. Med. J.*, II, 318, **1915**; Dakin and Dunham, "Handbook of Disinfectant."

[4] Cullen and Austin, *J. Biol. Chem.*, **34**, 553 (1918).

In actual experience a pure sodium hypochlorite solution at pH 8 begins to lose free oxygen to the air. The higher the temperature at this pH the more rapid is the decomposition. Coincident with this loss of oxygen the solution becomes more acid, and because of the increased acidity the decomposition is again hastened. It is an example of catalysis augmented by the hydrogen ion.

Whether or not it is the chlorine or the oxygen, or both, which are the active constituents of sodium hypochlorite, for every pound of chlorine used, one pound (100 per cent) of available chlorine is obtained in the product.

PREPARATION OF SODIUM HYPOCHLORITE

UNCHLORINATED SOLUTION—It was found desirable to use sodium hydroxide of good technical grade (60 per cent caustic ash) for chlorinating, and a good grade of soda ash (anhydrous sodium carbonate) for the buffer material. In order to make a solution of sodium hypochlorite of certain strength, a definite amount of alkali in the presence of the buffer will be required to maintain the stable point in pH. A stronger solution will require more alkali. The writer has made several thousand gallons of 2.5 to 5 per cent sodium hypochlorite during the last two years, and has found it desirable to maintain the concentration of sodium carbonate at the same point in all the formulas—viz., 2.5 per cent.

TABLE II SHOWING RELATIVE AMOUNTS OF ALKALI AND ALKALI CARBONATE FOR DIFFERENT CONCENTRATIONS OF PRODUCT

NaOH (60% Free Alkali)	Na_2CO_3 (Anhydrous Soda Ash)	Average Chlorine for Stable Product	pH (Approx.)
%	%	%	%
2.5	2.5	1.4	10.0
5.0	2.5	2.25	10.8
7.5	2.5	3.25	10.5
10.0	2.5	4.50	10.5
12.5	2.5	6.25	10.6

For 5 to 25-gallon quantities of hypochlorite, the alkali and soda ash are weighed into an iron or copper bucket, and about one-third to one-half of the water is added and the whole stirred until dissolved. It is then filtered through layers of absorbent cotton or muslin into the chlorinating receptacle, which should contain the remainder of the water.

CHLORINATION—The chlorine is led from a commercial drum through a copper tube fitted with a brass or bronze needle valve, and silver soldered thereto. The copper tube may be made to fit snugly into the valve head on the chlorine drum and clamped there under pressure. The copper tube from the needle valve terminates into a gas meter, which is chlorine-tight. The meter may be either of the dump type or Venturi effect. Both have been used with success. They must be made entirely of glass and filled with a nonfreezing, nonchlorine-attacking solution such as an alkali chloride brine (NaCl). If rubber connections are used they will have to be frequently replaced. A chlorine distributor for immersion into the alkali solution may be made from a coarse alundum thimble and glass tube. Similar diffusers are already on the market. By aid of the needle valve the stream of chlorine gas can be easily regulated. For large-quantity production the chlorine meter may be dispensed with, but it is then necessary to follow the rate of chlorination by titration.

CONTROL OF STRENGTH OF HYPOCHLORITE—It is only necessary to know the quantity of chlorine passing into the alkali during a given time interval to calculate the strength in terms of available chlorine. However, it is often more convenient to have available a 0.1 *N* sodium thiosulfate solution for the purpose of direct determination of the available chlorine content. The method used in this laboratory is to measure 10 cc. of distilled water, 5 cc. of glacial acetic acid, and 5 cc. of 5 per cent sodium iodide into a Erlenmeyer flask. Exactly 2 cc. of the hypochlorite solution are added, and the liberated iodine is titrated directly with the thiosulfate to the disappearance of the yellow color. No starch paste is necessary, although a white paper background is convenient.

The number of cubic centimeters of 0.1 *N* sodium thiosulfate required for the 2 cc. of chlorinated solution, multiplied by the factor 0.1772, will give the percentage of available chlorine in the sodium hypochlorite. The percentage of available chlorine multiplied by 1.05 is the percentage of sodium hypochlorite in the solution. It is very essential that the difference between the concentration of available chlorine and concentration of sodium hypochlorite be specifically stated. The two are often intermingled.

RELATIVE COSTS OF PRODUCTION

The overhead expense of this method of manufacture is very low. Soda ash and caustic soda are relatively cheap—the former is around 2 cents per pound, and the latter about 4 cents per pound. Drum chlorine is quoted at 7 to 10 cents per pound. Thus, if we allow 50 per cent for labor costs, the expense of producing 2.5 to 5 per cent "available chlorine" sodium hypochlorite amounts to approximately 6.80 cents and 16.22 cents per gallon, respectively. These values are in a marked contrast with the price of some of the commercial sodium hypochlorite preparations now on the market.

Dimensions of Beakers and Flasks

A conference on standardization of dimensions of glass beakers and flasks held at the Bureau of Standards January 28, 1922, was attended by representatives of the American Chemical Society, the Manufacturing Chemists Association, the Association of Scientific Apparatus Makers of the United States of America, several government departments, and each of the manufacturers of glass beakers and flasks in the United States. The discussion led to the approval of the selection of sizes recommended in the published report[1] of the Committee on Guaranteed Reagents and Standard Apparatus of the American Chemical Society. A definition of capacity was adopted that is in accordance with long-established custom in the glass-blowing industry. It provides that the vessels shall hold between 10 and 20 per cent over the nominal capacity. A subcommittee was appointed with authority of the conference to decide in detail on the dimensions. This committee consisted of representatives of the three associations named above and representatives of all the manufacturers.

It had been generally agreed that no radical changes in dimensions were desired. The changes needed were to permit better nesting of beakers where necessary for shipment and to correct the capacities of a few of the sizes which were not within the limits adopted. The expense involved in making a large number of changes would be all out of proportion to the benefit derived, because there has been little complaint in the past with reference to the dimensions of beakers and flasks.

The subcommittee had a meeting in New York to discuss the best way of coming to a decision on the different items. Data from the manufacturers were later compared and a tentative set of dimensions prepared for further consideration.

At a final meeting of the subcommittee held in Washington April 30, 1923, a modification of this set of dimensions was adopted. The manufacturers of beakers and flasks have proceeded to change their molds as required to bring the dimensions of the different articles within 1 or 2 millimeters of the standards set. The changes are in nearly every instance so slight that very few users will notice that any changes have been made. Vessels from different manufacturers will, however, be more nearly of the same size, beakers will nest better, and the relation between actual and nominal capacity will be more uniform. The exact dimensions selected can be obtained from the secretary of the subcommittee, W. D. Collins, U. S. Geological Survey, Washington, D. C.

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[1] THIS JOURNAL, **13**, 1070 (1921).

The University of Chicago has announced a gift of $200,000 from the Seymour Coman estate, the income to be used for "scientific research, with special reference to preventive medicine and the cause, prevention and cure of diseases."

The Titration of Sodium Formaldehydesulfoxalate[1]

By Bernard Salkin

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The alkaline copper sulfate method for the analysis of sodium formaldehydesulfoxalate (or of sodium hyposulfite) is an excellent one, because under the conditions of the experiment none of the impurities are oxidized, and therefore they do not appear in the result.

The iodine method, however, is not as good an indicator of the main product, because such impurities as sodium thiosulfate, sodium bisulfite, etc., will also consume iodine and indicate a larger percentage of the main product than is actually present. This is well indicated in Sample 5320, where the iodine method gave a result 10.8 per cent higher than that obtained by the copper method. This discrepancy may be explained by the presence of iodine-consuming impurities, and the nature of these impurities can be determined from an examination of the results obtained by calculation.

If in any case the iodine and copper percentages do not check, they must be so arranged that a result is obtained for iodine consumed, which represents only the sulfoxalate. This is necessary for the determination of the sodium bisulfite formaldehyde, since for this the difference between two titrations is used, in the second one of which the sulfoxalate consumes 50 per cent more iodine than in the first, while the amount of iodine consumed by the impurities does not change.

As late as February, 1922,[2] it has been claimed that it is practically impossible to titrate sodium formaldehydesulfoxalate by two different methods and obtain equivalent results. Furthermore, two very simple methods—that of titration with an alkaline copper sulfate solution, and an idiometric titration—are displaced in favor of more complicated methods. This can be explained by the fact that the procedure outlined by Jellinek[3] is not conducive to correct and uniform results. As the result of experimentation a method has been worked out which will not only give uniform results in the determination of the main product, but will also indicate the kind and the amount of the impurities present.

Just as with sodium hyposulfite, the titration of sodium formaldehydesulfoxalate can very easily—and best—be carried out by titrating its solution with strongly ammoniacal copper sulfate solution. The impurities present are not oxidized under the conditions of the analysis, the copper sulfate having a selective action on the sodium formaldehydesulfoxalate or the sodium hyposulfite.

Whereas in the case of the sodium hyposulfite only a small percentage of impurities is usually present, sodium formaldehydesulfoxalate may contain a large percentage of foreign substances—e. g., sodium bisulfite formaldehyde, sodium bisulfite, etc.

Of greater importance than the actual assay of the sulfoxalate is the knowledge of the nature of the impurities present, since the presence of sodium bisulfite formaldehyde seems to be one of the main causes of toxicity in the finished neoarsphenamine, when the former is used in its preparation.

It is indeed fortunate that there is a method which will give the assay of the pure substance, as well as indicate the character and amount of the impurities without resorting to any complicated procedure. All that is necessary is the titration of a sample in three different ways.

The author found that the method formerly used for determining the impurities was worthless. Jellinek's directions call for the addition of a large excess of sodium bicarbonate and vigorous shaking while titrating to a yellow color with 0.1 *N* iodine solution. The results of a series of blank experiments, using only sodium bicarbonate and water, showed that the amount of iodine absorbed was directly proportional to (1) the amount of bicarbonate used, (2) the length of time that the iodine was in contact with the bicarbonate, and (3) the amount of iodine added in excess; and was also dependent on the amount of shaking.

The method which follows is one that will not only check itself, but also allows interpretation of the results.

Method

Preparation of Solutions—*Solution 1.* Dissolve about 500 grams copper sulfate crystals in 2 liters distilled water; add 1600 mls. 28 per cent ammonia water and make up to 4 liters with water. This solution is assayed for copper either electrolytically or by the method outlined by Sutton.[4]

Solution 2. A 0.1 *N* sodium thiosulfate solution, standardized by any of the usual methods.

Solution 3. A 0.1 *N* iodine solution checked against a standard sodium thiosulfate solution at each titration. In addition to these solutions an approximately 10 per cent caustic soda solution and 28 per cent (stronger) ammonia water are required.

Procedure—*First Titration.*

Notes: (1) The entire procedure must be carried out under anaerobic conditions; the sulfoxalate solution must always be kept under an atmosphere of nitrogen.

(2) Only recently boiled distilled water should be used throughout.

Weigh out 15 grams of sample to be analyzed, put into a 100-ml. volumetric flask, add water, dissolve, and make up to mark. (Call this Solution A.)

Into a 250-ml. volumetric flask place 10 ml. of Solution A and make up to the mark with water. (Solution B.)

Into a wide-mouth, 250-ml. Erlenmeyer flask provided with a 3-hole cork stopper, through one hole of which passes an L-tube reaching to about 1.5 inches above the bottom of the flask, put 50 ml. of Solution 1 and 40 ml. of 28 per cent ammonia water. Warm the mixture to 55° C., and keep at this temperature by means of a hot plate or a water bath. While passing in a stream of nitrogen through the L-tube, titrate the copper solution with Solution A until the mixture is colorless. Repeat this titration in order to check the result.

If the percentage of sodium formaldehydesulfoxalate is low, only 30.0 ml. of ammoniacal copper sulfate solution and 25 ml. of ammonia water are used.

Calculation: 1.00 ml. ammoniacal copper sulfate solution containing 0.07982 gram copper sulfate is equivalent to 0.0295 gram sodium formaldehydesulfoxalate.

Second Titration. Flush a 250-ml. Erlenmeyer flask with nitrogen. Run into it 25.0 ml. of the Solution B, and immediately add 0.1 *N* iodine solution until the end point is reached. Add 2.0 ml. of iodine solution in excess, allow to

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[1] Received March 16, 1923. Presented before the Division of Industrial and Engineering Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Heyl and Greer, *Am. J. Pharm.*, **94**, 80 (1922).

[3] Jellinek, "Das Hydrosulfit," Teil 2, p. 100.

[4] "Volumetric Analysis," 9th ed., p. 188.

stand for 5 minutes, and titrate back with the 0.1 *N* sodium thiosulfate solution.

Calculation: On the basis of the number of milliliters of iodine solution consumed, 1.00 ml. 0.1 *N* iodine solution is equivalent to 0.00295 gram of sodium formaldehydesulfoxalate.

Note: This result should check very closely with that obtained by the first titration ("Copper" method).

Third Titration. Flush a 250-ml. Erlenmeyer flask with nitrogen. Run into it 25.0 ml. of Solution B, and immediately add 0.1 *N* iodine solution in amount equal to 50.0 ml. more than was used in the second titration. Then add 10 per cent sodium hydroxide solution until the color of the mixture is a light yellow. Allow to stand 10 minutes. Acidify with dilute hydrochloric acid, and titrate the liberated iodine with 0.1 *N* sodium thiosulfate solution.

Calculation: From the number of milliliters of iodine solution consumed in this titration, subtract one and one-half times the number of milliliters of iodine solution consumed in the second titration. Each milliliter of 0.1 *N* iodine solution in the difference is equivalent to 0.00335 gram of sodium bisulfite formaldehyde.

From the results, we have the percentage of sodium formaldehydesulfoxalate (checked by two methods) and the percentage of sodium bisulfite formaldehyde.

ANALYSIS OF SULFOXALATES

A number of sulfoxalates were analyzed and the results were tabulated as follows:

SODIUM FORMALDEHYDESULFOXALATE

Sample	Copper Method	Iodine Method	Sodium Bisulfite Formaldehyde
5320	72.7	83.5	....
5368	31.4	31.4	53.25
5367	75.6	75.9	7.25
5554	17.4	17.7	66.0
5584	26.2	26.35	61.25
5575	23.8	23.95	59.9

The discrepancy in the first sample between the percentages for sulfoxalate obtained by the copper and the iodine methods is explained only by the presence of an impurity other than sodium bisulfite formaldehyde. This impurity must be sodium hyposulfite, for if we assume that any other impurity—e. g., sodium bisulfite—is present, the total of the percentages is above 100 per cent. Then, again, sodium hyposulfite could easily have been formed if insufficient formaldehyde had originally been added, or if much had been lost by evaporation.

The calculation is as follows:

$$Na_2S_2O_4 + 2CuSO_4 + 4NH_4OH \rightarrow Na_2SO_3 + Cu_2SO_4 + (NH_4)_2SO_3 + (NH_4)_2SO_4 + 2H_2O$$

$$NaHSO_2.CH_2O + CuSO_4 + 3NH_4OH = Na(NH_4)SO_3 + CH_2O + Cu_2SO_4 + (NH_4)_2SO_4 + 2H_2O$$

Thus:

1 $CuSO_4$ = $^1/_2$ hyposulfite or $^1/_2$ sulfoxalate or 1 norm $CuSO_4$ = $^1/_4$ mol hyposulfite or $^1/_4$ mol sulfoxalate

For the iodine titration:

$$Na_2S_2O_4 + 6I + 4H_2O = 2NaHSO_4 + 6HI$$
$$NaHSO_2.CH_2O + 4I + 2H_2O = NaHSO_4 + CH_2O + 4HI$$

Thus:

1 mol iodine = $^1/_6$ mol hyposulfite or $^1/_4$ mol sulfoxalate

Then if x = grams of sodium hyposulfite in the entire solution and y = grams of sodium formaldehyde hyposulfite in the entire solution

$$\text{For the copper titration } \frac{x}{43.5} + \frac{y}{29.5} = a$$

$$\text{For the iodine titration } \frac{x}{29} + \frac{y}{29.5} = b$$

where

a = norms of copper sulfate used in titration
and b = norms of iodine used in titration

Thus, for Sample 5320:

	Per cent
Sodium hyposulfite	30.6
Sodium formaldehydesulfoxalate	52.0
	82.6

ACKNOWLEDGMENT

This work was done in the research laboratory of E. R. Squibb & Sons, during the early part of 1922, while making an investigation of neoarsphenamine and its manufacture.

To Consumers of Pure Chemicals

Representatives of twenty-seven medical, pharmaceutical, scientific, and engineering societies in conference in Pittsburgh recently passed the following resolution: "It is the sense of this meeting that we favor the gradual adoption of the metric system wherever practicable."

The Council of the AMERICAN CHEMICAL SOCIETY has put itself on record in favor of the purchase of pure chemicals and of apparatus exclusively in metric units. All the bureaus of the United States Government are buying their pure chemicals exclusively on a metric basis. Large firms are selling their pure chemicals exclusively in metric units. Two hundred colleges and universities and three hundred firms have agreed to buy their pure chemicals and apparatus on metric specifications.

About 50,000 "stickers" have been distributed without charge insisting that "orders must be filled and billed in metric units." Some dealers have boasted of the fact that on telling customers that there might be a delay in supplying metric packages, the customers professed not to care whether English or metric packages were used. Naturally, we are not going to get anywhere in our campaign if we do not *insist* on getting metric packages even when it means some inconvenience. Therefore, please insist on getting what you want—viz., metric packages, without any delay caused thereby or any additional cost. You can get it. Once started in the campaign to have all pure chemicals bought and sold in metric units we must see it through to the finish. Only a small part of that limited task is accomplished as yet. Failure would be a bad setback to the whole metric idea. Success will furnish a valuable object lesson for the further advances.

The Metric Association has agreed to give to this committee for its work 90 per cent of dues received from memberships in that association obtained by it. The committee has obtained several such memberships and has thus started a regular income for its work. Many more members are needed, however. Individual memberships are $2.00 and corporation or firm memberships $10.00.

There is much to be done in securing adequate teaching of the metric system in the schools and in securing double marking of bottles, boxes, cans, collars and shirts, automobile tires, etc. Doctors need to be encouraged to write prescriptions in metric units so that the druggists can throw away the antiquated apothecary weights.

1—Will you buy your pure chemicals in metric units this year?
2—Have you encountered any difficulty in obtaining metric packages promptly and reasonably?
3—Can you use any stickers, and if so, how many?
4—Will not you or your firm join the Metric Association?
5—Can you suggest some activity in favor of the metric system which you will undertake in your locality?

E. C. BINGHAM, *Chairman*
Committee on Metric System of the A. C. S.

LAFAYETTE COLLEGE
EASTON, PA.
June 25, 1923

The Viscosities of Mixtures of Sulfuric Acid and Water[1]

By F. H. Rhodes and C. B. Barbour

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This investigation was undertaken for the purpose of verifying the results of previous work on the viscosities of mixtures of sulfuric acid and water. The procedure for the determination is described and the results are shown both in tabular and graphic form. The results are compared with those of earlier investigators, and a discussion of the practical application of these resutls is included.

The viscosities of mixtures of sulfuric acid and water have been determined by Graham,[2] Wagner,[3] and Dunstan and Wilson.[4] The measurements made by Graham were at a single temperature only (20° C.), while the determinations by Dunstan and Wilson were all made at 25° C. Wagner determined the viscosities at temperatures of 15°, 25°, 35°, and 45° C., but he used only three mixtures, containing, respectively, 23.4, 15.5, and 7.87 per cent of sulfuric acid.

Obviously, the results obtained by these earlier investigators give little information as to the effect of temperature upon the viscosities of solutions of sulfuric acid. Moreover, these earlier results do not agree very well among themselves. The values obtained by Dunstan and Wilson are very much higher than those given by Wagner for solutions of similar concentrations and at the same temperature. Graham and also Dunstan and Wilson observed a maximum in the viscosity-concentration curve at a point corresponding to the composition of the hydrate H_2SO_4-H_2O; but Dunstan and Wilson observed a minimum in the curve between this point and the point corresponding to the composition of pure H_2SO_4, while Graham observed no such minimum.

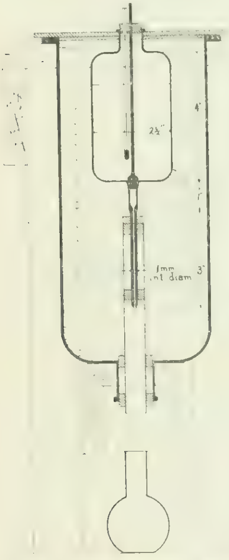

Fig. 1—Viscometer for Determination of Viscosities of Mixtures of Sulfuric Acid and Water

Experimental

The viscometer used in this work consisted of a cylindrical glass bulb with a capacity of about 200 cc., provided with a tubulature at the top and terminating at the bottom in a glass capillary tube which was 8 cm. long and 1 mm. in internal diameter. A glass valve, mounted on a glass rod, was ground in to close the passage between the bulb and the lower capillary tube. The upper tubulature was fitted with a cork stopper which was provided with an air vent, through which were inserted the thermometer for indicating the temperature of the liquid within the bulb and the glass rod which served as the stem of the cut-off valve at the bottom of the bulb. The viscometer was supported, as shown, in an inverted bell jar, which served as a constant temperature water jacket, the apparatus being so arranged that both the bulb and the capillary were maintained at the temperature of the water within the bath. The water in the water bath was heated by live steam, when necessary, and was stirred by a slow current of air.

In making a determination of viscosity, the liquid to be tested and the water in the water bath were heated separately to the temperature at which the determination was to be made. The liquid was then placed in the viscometer bulb, and both the liquid in the bulb and the water in the water bath were brought to the desired temperature and maintained at this temperature throughout the determination. When the temperature was adjusted properly, the valve was lifted and liquid was allowed to flow from the bulb until the capillary was filled and the meniscus at the top of the liquid stood exactly at the level indicated by a fixed mark around the bulb. A graduated flask, containing exactly 63.6 cc., was then placed below the capillary, the valve was lifted to a definite height, and the time required for the outflow of exactly 63.3 cc. of the liquid was determined.

The viscometer was calibrated by determining the times of flow of several liquids of known kinematic viscosity, and from these results a calibration curve for the instrument was drawn (Fig. 2). The liquids used in calibrating the viscometer were water, benzene, linseed oil, 20 per cent sucrose solution, 40 per cent sucrose solution, and various petroleum oils. The values for the viscosities of benzene and of linseed oil were taken from the Smithsonian Tables, those for the viscosities of water and the sucrose solutions were those

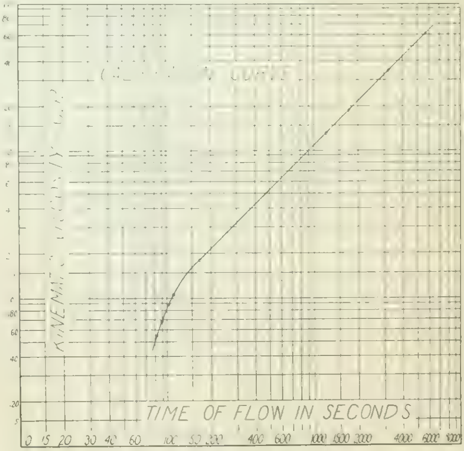

Fig. 2—Calibration Curve

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[1] Received March 26, 1923.

[2] Graham, *Trans. Roy. Soc. London*, **151A**, 373 (1861).

[3] Wagner, *Ann. Physik*, **18**, 259 (1883).

[4] Dunstan and Wilson, *J. Chem. Soc.* (*London*), **91**, 83T (1907).

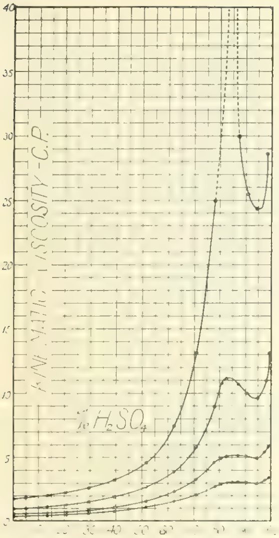

FIG. 3—KINEMATIC VISCOSITIES

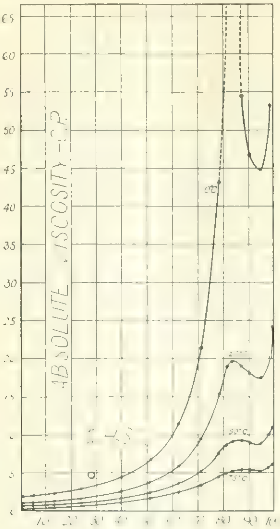

FIG. 4—ABSOLUTE VISCOSITIES

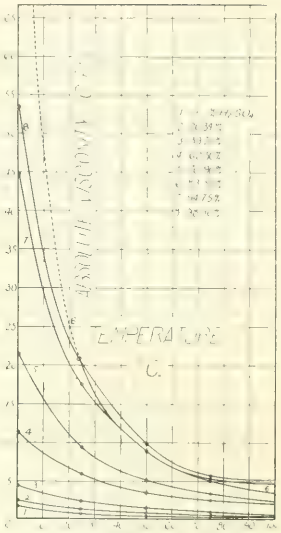

FIG. 5—CHANGES OF VISCOSITY WITH TEMPERATURE

given by Bingham and Jackson.[5] The viscosities of the petroleum oils were determined by means of a Saybolt Universal viscometer, the Saybolt seconds being translated into centipoises by the use of a conversion diagram drawn from the data given by Herschel.[6]

The mixtures of sulfuric acid and water were prepared from pure distilled water and pure 95 per cent sulfuric acid, or from 95 per cent sulfuric acid and pure fuming sulfuric acid. The percentage of sulfuric acid in each of the mixtures was checked by titration with standard alkali.

These results are shown in the table and also graphically by the accompanying curves. Fig. 3 shows the kinematic viscosities, Fig. 4 the absolute viscosities.

DISCUSSION OF RESULTS

The general form of these viscosity-composition curves is similar to that of the curve obtained by Dunstan and Wilson. Their curves agree with those of the authors in showing

VISCOSITIES OF MIXTURES OF SULFURIC ACID AND WATER AT VARIOUS TEMPERATURES

H_2SO_4 Per cent	Time Sec.	Kinematic Viscosity Cp.	Density G./Cc.	Absolute Viscosity Cp.	H_2SO_4 Per cent	Time Sec.	Kinematic Viscosity Cp.	Density G./Cc.	Absolute Viscosity Cp.
		Viscosities at 0° C.					*Viscosities at 50° C.*		
0.00	167.0	1.80	0.999	1.80	0.00	82.5	0.562	0.988	0.556
5.00	176.0	1.90	1.038	1.97	5.00	84.2	0.60	1.028	0.62
9.39	182.7	1.97	1.068	2.10	9.39	87.0	0.64	1.054	0.68
13.42	192.0	2.05	1.100	2.26	13.42	89.5	0.67	1.078	0.72
17.42	199.5	2.14	1.132	2.42	17.42	91.9	0.71	1.105	0.78
20.34	211.0	2.27	1.155	2.62	20.34	94.4	0.76	1.124	0.85
24.10	231.4	2.50	1.184	2.96	24.10	98.3	0.83	1.152	0.96
29.80	256.0	2.75	1.230	3.39	29.80	105.5	0.94	1.196	1.12
39.70	318.8	3.40	1.316	4.47	39.70	124.6	1.25	1.280	1.60
51.20	419.3	4.50	1.523	6.85	51.20	154.3	1.63	1.486	2.42
62.50	692.0	7.50	1.543	11.56	62.50	219.3	2.40	1.501	3.53
70.90	1222.3	13.20	1.640	21.60	70.90	307.5	3.30	1.596	5.26
78.20	2277.0	25.00	1.727	43.20	78.20	417.3	4.50	1.679	7.55
81.40	Solid at	0° C.			81.40	462.0	5.00	1.714	8.57
83.50	Solid at	0° C.			83.50	484.0	5.20	1.734	9.08
87.50	2477.0	30.00	1.820	54.60	87.50	478.5	5.20	1.770	9.18
90.30	2358.5	52.50	1.838	46.80	90.30	469.5	5.05	1.788	9.03
94.75	2220.0	24.20	1.855	44.80	94.75	467.0	5.00	1.807	9.03
98.30	2640.0	28.75	1.858	53.40	98.30	516.0	5.55	1.811	10.05
99.60	Solid at	0° C.			99.60	551.0	6.00	1.808	10.80
		Viscosities at 25° C.					*Viscosities at 75° C.*		
0.00	105.0	0.94	0.997	0.94	0.00	72.8	0.40	0.974	0.39
5.00	107.7	0.98	1.033	1.01	5.00	73.6	0.43	1.023	0.44
9.39	112.0	1.05	1.061	1.11	9.39	75.5	0.46	1.045	0.48
13.42	116.0	1.05	1.061	1.22	13.42	77.2	0.48	1.065	0.51
17.42	120.6	1.20	1.120	1.34	17.42	78.5	0.51	1.098	0.56
20.34	125.0	1.25	1.139	1.41	20.34	80.6	0.54	1.109	0.60
24.10	131.5	1.35	1.168	1.58	24.10	83.5	0.58	1.136	0.66
29.80	145.0	1.55	1.213	1.88	29.80	87.8	0.65	1.178	0.77
39.70	177.0	1.90	1.300	2.46	39.70	100.0	0.85	1.262	1.07
51.20	229.5	2.48	1.504	3.73	51.20	119.2	1.18	1.467	1.72
62.50	352.5	3.90	1.522	5.93	62.50	156.6	1.70	1.481	2.52
70.90	545.5	5.90	1.618	9.45	70.90	203.5	2.20	1.574	3.42
78.20	843.2	9.10	1.703	15.50	78.20	252.5	2.70	1.654	4.46
81.40	990.0	10.8	1.739	19.00	81.40	271.0	2.90	1.689	4.90
83.50	1020.0	11.2	1.760	19.70	83.50	282.0	3.03	1.709	5.17
87.50	990.0	10.8	1.795	19.00	87.50	284.0	3.04	1.744	5.32
90.30	925.5	10.0	1.813	18.13	90.30	281.0	3.03	1.764	5.35
94.75	885.0	9.6	1.831	17.60	94.75	280.0	3.00	1.782	5.35
98.30	1017.0	11.0	1.835	20.20	98.30	296.0	3.20	1.788	5.72
99.60	1217.0	13.2	1.832	24.20	99.60	315.0	4.30	1.785	6.06

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[5] *Bur. Standards, Sci. Paper* **298**.

[6] *Bur. Standards, Tech. Paper* **112**.

maxima at 84.5 per cent and 100 per cent sulfuric acid, corresponding to the compositions of the compounds $H_2SO_4.H_2O$ and H_2SO_4, respectively, and a minimum at 94.5 per cent sulfuric acid. The viscosities found by the authors are, however, very much lower than those found by Dunstan and Wilson for mixtures of the same composition. For example, according to the authors the mixture containing 84.5 per cent sulfuric has an absolute viscosity of 20 centipoises, while Dunstan and Wilson give, for the same mixture, a viscosity of 94 centipoises. The results for the viscosities at 25° C. agree substantially with the results obtained by Wagner at this same temperature.

It will be observed that the maxima and the minimum are much less pronounced at 75° C. than at the lower temperatures, which seems to indicate that the hydrate complexes to which the viscosity of the more concentrated solutions is due are largely dissociated at the higher temperature. This hypothesis is supported by the fact that the rate of decrease of viscosity with increasing temperature is very much greater with the concentrated solutions than with the dilute solutions, owing to the superimposed effects of two factors—the normal increase in fluidity, and the increasing dissociation of the hydrate complexes. These changes in viscosity with the temperatures are plotted in Fig. 5.

The results obtained for the viscosities of mixtures of sulfuric acid and water are not only of general scientific interest, but are also of value in calculating the rates of flow of such mixtures through pipes, using the modified Fanning formula given by Wilson, McAdams, and Seltzer.[6] They have also a very direct application in the explanation of the effect of temperature upon the performance of the lead storage cell. Further work on the viscosity of fuming sulfuric acid is in progress.

[6] This Journal, **14**, 105 (1922).

Tungsten Wire for Hydrogen-Ion Determinations[1]

By John R. Baylis

Baltimore City Water Department, Baltimore, Md.

HYDROGEN-ION tests are now regarded as a necessity in an increasing number of industries, due to its giving indication of certain stages of chemical reactions. This is leading to the demand for instruments that will automatically record the pH changes. While the hydrogen electrode gives an accurate measurement of the hydrogen-ion concentration of many solutions, the method of making such determinations and the care necessary for accurate results make it difficult to construct a machine that will constantly indicate the pH. If the use of hydrogen gas could be eliminated, one very troublesome element would be removed.

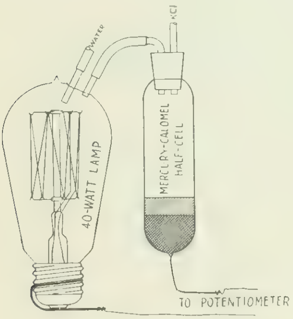

Fig. 1—Tungsten Lamp Electrode

Most efforts heretofore have been to develop an electrode that will give the hydrogen-ion concentration of most any solution by producing the same voltages—that is, an electrode where 0.8 volt will mean the same concentration for any solution regardless of its nature. This would be the ideal electrode, but such exacting demands are not necessary for many uses. Assuming the ideal to be impractical, the next best thing is one that will give voltage differences that are indicative of pH changes in the solution. If 0.4 volt in one solution indicates a pH of 7.0 and 0.8 volt in another indicates the same pH, there should be no great difficulty in applying such conditions to the industries, provided pH changes produce voltages that are readily measurable. If a certain solution gives a voltage of 0.3 at a temperature of 10° C. and 0.4 at a temperature of 30° C., this is not serious so long as the temperature effect is known. Voltage differences due to the constituents of the solution are not serious so long as the substance being added, or being changed, will produce differences that are readily measurable and indicative of certain reactions.

With the hope of developing an electrode that does not require the use of a gas and that may be used to indicate pH changes produced by the application of chemicals for purifying Baltimore's water supply, the author has tried several metals in connection with the mercury-calomel half-cell. It was found that the tungsten wire in an ordinary 40-watt electric lamp gives such uniform results within certain pH ranges as to be suggestive of being useful for such work. The maximum range of the water since the tests were started three months previous to this writing has been pH from 6.5 to 8.6. The useful range may not extend greatly beyond these figures, but this covers a very important range. There is a voltage difference of approximately 0.09 for each

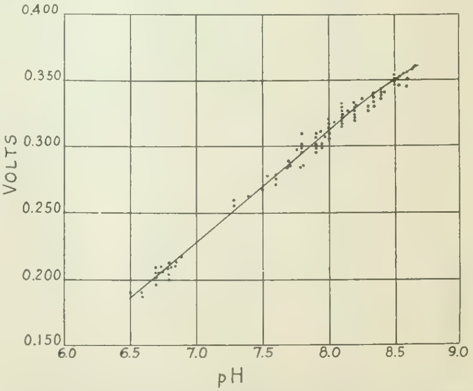

Fig. 2—Relation of Voltage to pH When Using a 40-Watt Tungsten Lamp. pH Determined Colorimetrically. Gunpowder River Water Used. Temperature Approximately 10° C.

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[1] Received May 5, 1923

pH, which is considerably more than the hydrogen electrode. The electrode has been tried only on this particular water, and there is no assurance that it will work on others. There is also no assurance that it will give accurate results under all conditions of the water tried, but there have been considerable changes during the three months duration of the test with no appreciable change in the results.

Fig. 1 shows the electrode. A hole was ground into the light globe large enough for two small tubes, one for the potassium chloride solution and the other for the water. A rapid displacement of the water gives best results. Fig. 2 shows curve plotted from a number of determinations made from several different lamps. The pH was determined by color standards. A lamp will give accurate results for about a week, then there might be a gradual deviation from the first readings.

The elimination of gas and the simplicity of such an electrode make it of great value if it has a fairly wide range and proves as reliable as experiments now indicate. The author does not have time to test its usefulness beyond his own particular condition, and is making this public with the hope that others will investigate its possibilities.

The Efficient Recovery of Nitrates from Caliche[1]

By J. W. Turrentine

Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

THE many reports appearing in the current press relative to the present situation in the nitrate industry of Chile all give substance to the impression that conditions there are far from ideal. The situation is confused, to be sure, with various elements, such as local politics, finance, and international commerce, but evidence remains that the trouble is fundamentally one of poor chemical engineering. For this conviction one need go no further than the recent publications of Allen and the report of Donnan.

Suggested Remedies for Chilean Nitrate Situation

The nitrate industry is experiencing the results of the total loss of an important part of its market, Germany, cut off by blockade during the war and now on an entirely self-supporting basis through the war-time development of its air nitrate industry. It is faced with the loss of other markets through a similar development of the air nitrate industry in the various countries now buying Chilean nitrate. This is notably true in the United States, where it is scarcely conceivable that we shall delay much longer in taking this important step toward national self-sufficiency. This move, carried to its logical conclusion, among the nitrate-using nations of the world will deprive the nitrate industry of its markets and will result in the destruction of that industry. While not immediately probable, it is still quite possible and offers a disturbing consideration. It is inevitable that such a contemplation will act as a depressant; likewise, that the question will be asked and must be answered. "What can be done about it?"

The answer is obviously: "Cheapen the product; first to eliminate the incentive to develop air nitrate industries in other countries, and second, to make it more difficult for air nitrates to compete."

The cost of producing and selling Chile nitrate has been apportioned as follows:

	Per cent
Export tax	41
Bags	6
Transportation	11
Overhead	3
Labor	19
Fuel	11
Interest	9

The inevitable reaction to the suggestion that the price be lowered is, first of all, to look to the Chilean government for a reduction of taxation. In this case the tax is principally the export tax imposed by that government, which may be reduced on the nitrate industry by distributing it over other industries notably the copper industry.

Another suggestion is to increase the pro-nitrate propaganda in foreign countries—first, to increase the use of nitrates, and second, to combat hostile legislation.

As is generally the case, the last suggestion to be acted upon is the one that plants and processes be modified and brought up to date to cheapen the production costs and place the industry at once on a sounder and more economic basis.

Such a suggestion calls for the reconstruction of plants, and that for an outlay of capital, and, as is generally the case in an industry facing adversity, capital is hard to secure and at best is secured at a high cost. The price of money is frequently measured by the acuteness of the distress of the borrower and in the same ratio. In the past, profits have been dissipated in the payment of large dividends and no surplus seems to remain for developments.

But even where capital is abundant, it is extremely difficult to persuade manufacturers to forsake methods of operation that have yielded profits in the past for new and, to them, strange processes, even where the promise of greatly increased profits is extended. Such changes extend beyond finance and plant and apparatus to include organization, for an organization trained to operate one process may be "green hands" when applied to a new one.

The Chilean nitrate deposits have been of the utmost importance to the world and it is not certain that the end of that importance is at hand. The increased recovery of by-product ammonia in America, for example, will decrease still further our demand for nitrates, although in Germany the coking of coal exclusively in by-product ovens did not serve to terminate the importation of nitrates and still left a deficit to be met through the manufacture of air nitrates; and there the use of concentrated fertilizers is more largely developed than here.

In addition, there is a further possibility that America may be led to adopt that most vital economy of substituting by-product coke for bituminous coal for domestic and industrial use, and in that way abolish the present highly reprehensible and indefensible practice of burning raw bituminous coal. This would enormously increase the output of by-product ammonia for fertilizer purposes and the other great quantities of valuable materials produced therewith, instead of devoting them, as at present, to the pollution of our atmosphere and the consequent impairment of our health and happiness. To further such a worthy economy we might well rigidly exclude the competition of nitrates from all foreign sources.

Although it is still obtaining its main supply there, this country is no longer dependent on Chile for its iodine, for it has been dem-

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[1] Received March 22, 1923. Presented before the Division of Industrial and Engineering Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

onstrated that an adequate quantity can be yielded through the development of the kelp industry.

It is evident that the perpetuation of the Chilean industry is not essential to America, but it is not certain that its destruction will not prove a great economic loss to the world in general, and it is certain that its destruction would be a national calamity to the Chilean people. In that fact, certainly, is found an adequate reason for any measures, however drastic, which will insure the continued functioning of the industry. It is essential that everything be done that will count towards the neutralization of the present varied adversities confronting the industry. Government ownership and operation has already been suggested as a possible outcome of the present failure of private ownership to meet the situation. Researches financed by the government looking to the improvement of processes might forestall and obviate the necessity of more drastic steps.

Great improvement in the situation could be made in three directions:

> The government might surrender its export tax, thus reducing the price in the market by that substantial amount. To meet the necessity for government revenue, tax might be levied on private property, now largely exempt.
>
> Plants and processes could be improved so as to reduce the manufacturing costs. If capital is not readily available, it could be furnished by the government with the enforced amalgamation of small properties into larger groups, thus greatly reducing the cost of rehabilitation. (The prosperity of the Chilean government is so intimately linked with that of the industry that the two cannot be separated.) With new processes could be yielded by-products now imperfectly exploited.
>
> Propagandizing activities in foreign countries could be enlarged to enhance the use of nitrates, thus to increase and strengthen the market; to educate the agriculturists in its use and benefits; to meet its critics; to prevent its abuse; and to defend it against its opponents.

Inefficiency of Present Process

The one present by-product, iodine, capable it seems of very greatly increased production, is imperfectly presented with the single idea of maintaining the present high, monopolistic price totally without regard to obvious greatly increased markets if offered at a reduced price, and apparently without investigation of possible new uses for iodine. At present a portion of the iodine available is delivered to a selling agency which accepts only that quantity which can be absorbed by the market at a fancy price, being content with the large profits accruing to them from a practical monopoly and without intelligent interest in the prosperity of the producers.

The fact is clearly established that the processes now in operation are decidedly out of date. The lack of progress of the present operators is severely arraigned. It is shown that the methods now in vogue have been used for about forty years without material improvement, and have thus, to date, failed to utilize the modern developments in the science of chemical engineering; that of the available raw material at hand only the best is taken, representing a very inefficient usage of the deposits; that of the material taken very imperfect recoveries are made, a large portion of the nitrates originally present being thrown on the dumps and lost; that the methods applied to this imperfect recovery are expensive in both labor and fuel; and that imperfect control is maintained so that there is only a partial realization of the losses incurred.

More specifically, it is shown that the raw material is sorted, even hand-picked, and only the best grade is sent to the refinery, thus certainly reducing the average to a point below which the remaining material cannot be economically worked by present methods; that this is imperfectly, unevenly crushed, which precludes uniform and efficient leaching; that the grinding is carried out in such a way as to create large volumes of dust, which are blown away and lost, damage the machinery, and add to the discomfort and ill health of the employees; that the leaching is accomplished by gravity percolation, which is slow and because of inevitable channeling is imperfect; that a large quantity of slimes is washed through with the solution and represents a problem in itself, so far unsolved—a result of imperfect filtration; that while leaching is in progress the solution is so heated that evaporation takes place simultaneously, connoting a state of affairs where conditions are maintained unfavorable to both evaporation and solution; that leaching being imperfect, the material undergoing extraction is discharged still containing a large percentage of values (the estimated recovery is about 55 per cent); that obviously there is no practical way whereby the material may be continuously sampled to show whether extraction is complete or not; that the leaching vats are discharged by manual labor; that the steam used to heat the vats is employed without regard to the efficiency of its employment; that the hot solution discharged from the leaching vats is permitted to cool in transit largely by conductance instead of by evaporation, the maximum available work of the heat thus not being utilized; that the further cooling of the brine for the crystallization of the nitrates takes place slowly and likewise by conductance, since the formation of protective pellicles of crystals over the surfaces of the unstirred volumes of brine prevents evaporation; that while air cooling is used, no advantage is taken of the evaporative powers of the peculiarly dry, hot air of the region; that while the economical use of water is important, no effective effort to conserve water is made; that while fuel oil is expensive, no particular thought is given to the conservation of heat; that separation of the valuable potassium nitrate from the sodium salt is ignored and instead the two are sold together as the less valuable, and, in general, but little attention is paid to by-products; that no attention is paid to the elimination of borax, but instead that deleterious substance is permitted to contaminate the product; that the mother liquors are used without any great regard for solubility and solution efficiencies; and, in general, mechanical devices for the elimination of manual labor are neglected.

The solution with which the raw material is being leached is boiled while the leaching is taking place. The boiling is continued until a sufficiently concentrated solution is obtained, the concentration being attained by evaporation probably as much as by the taking up of more nitrate. Furthermore, what is worse, the solution is "purged" of impurities—that is, the less soluble substances are crystallized by evaporation or by a salting-out process, or probably both, while still in contact with the caliche from which it is supposed to be dissolving additional nitrate. So here is a condition where solution is supposed to be taking place—at any rate, an operation is being performed to bring about the solution of nitrate from caliche—while at the same time crystallization of salts and the evaporation of the solvent are being induced.

Let us analyze this intricate operation. A lump of caliche rich in nitrate is brought into contact with solution already heavily charged with saline material (nitrate and impurities). On the surface and within the interstices of the lump, nitrate dissolves to saturation, to the point where salting out of the less soluble ingredients is necessary before more nitrate can dissolve. Salting out occurs, and it occurs at the point where nitrate is dissolving. The formation of a coat or plug of crystals thus results, effectually preventing further solution, and the operation stops. In other words, no regard is given the elementary principle that materials dissolve only with difficulty in solution with which they form precipitates.

It is practically certain that with the impurities thus salted out a large portion of the potash is eliminated.

Possibilities of Improvement

The ideal process of recovering nitrate from caliche is one which obviates all the objections to the present archaic process. Is there such an ideal process?

Distance from the scene of operations, while regarded as an objection in that it relegates any proposed process to the class of "paper process of an author or would-be inventor," yet has the possible advantage that mountains appear as mole hills and that if the distance be great enough, difficulties which at close range appear insurmountable come to appear as no problem at all. A clear understanding of the elements of a problem is essential to the precise solution of that problem, but at the same time some perspective is likewise essential. It is clear that those most intimately associated with the industry are the ones most nearly completely overwhelmed by the obstacles in the way of improvement and are the least able to do anything about it. They cannot see the problem for the details; they refuse to be convinced because they do not admit the authority of their critics. To them authority is synonymous with familiarity. Yet, all constructive suggestions come from outsiders.

It is evident, therefore, even if a lack of intimate knowledge encourages the recommendation of palliatives that may not work, it is equally true that a too intimate knowledge may be quite as bad as inducing the inclination to condemn without trial. It is no more of a sin to propose something that may not work than it is to condemn something that will. An operator cannot escape his responsibility for condemning a proposed improvement in process by pointing out the imperfections of the one making the proposal. The merits of the case cannot be settled on the basis of personalities.

A process which obviates all the objections pointed out above as existing in the present mode of operation in the nitrate fields has already been worked out in all the essentials, and has been demonstrated by several years of actual operation—but not on caliche; otherwise, of course, there would be no problem. In any new application adjustments have to be made in details. This process is based on the most advanced methods of countercurrent leaching, filtration, and fractional crystallization. It is a process which admits of high capacity, continuous and automatic operation, and is highly conservative of fuel, water, power, and labor. It admits of simple and complete chemical control, and affords means of obtaining main and by-products of desired states of purity.

This method of grinding, lixiviating, evaporating, crystallizing, and treatment of mother liquors is being described in detail in the current series of articles, "Potash from Kelp,"[2] now appearing in THIS JOURNAL, and will not be further described here.

It has been shown that the main difficulty in the way of the acceptance of improved methods of plant processes in the nitrate field is the fear of the development of slimes. In other words, the difficulties in the past of handling solutions containing colloidal or near colloidal suspensions of clay have prevented the adoption of any modification in leaching methods looking to more rapid or more thorough leaching. Modern leaching practice prescribes a fine state of subdivision of the solids to be leached and thorough agitation with the solvent. This will tend to increase the proportion of slimes; but modern practice in the successful treatment of slimes and colloids of a wide range of characteristics convinces one that here is no insurmountable problem.

It is obvious that if caliche can be percolated without the liberation of slimes, it can likewise be filtered without the liberation of slimes, provided the coarser particles of mineral matter naturally present therein are employed as a matrix wherewith to retain the finer particles. This may be done rapidly with rotating filters where the filter cake is removed before it has reached an impervious thickness. The prevailing impression that rotating vacuum filters cannot be used in the industry apparently is due to the fact that they have been applied only to the removal of slimes alone, and not to the filtration of the natural mixture of fine and coarse particles of earthy materials making up the caliche. The filtration of clayey soils and even of colloidal clay in this laboratory is no longer an unsolved problem.

Countercurrent lixiviation of a finely ground caliche with adequate agitation with the solvent will afford a completely extracted solid as one product and a hot, practically saturated solution as the other. It may be applied to low-grade materials as well as high-grade.

Caliche of 18 per cent nitrate content is regarded as the lowest grade material that can now be profitably processed by the present antiquated methods. If this is the limit with a recovery of 55 per cent efficiency, it is obvious that with a recovery of 99 per cent material as low in nitrate content as 10 per cent can be used without regard to any other economies obtained. This alone will mean a tremendous increase in the quantities of workable caliche available.

Steam evaporators give rapid, controlled, and cheap evaporation, and vacuum crystallization affords advantages not possessed by any other method. It permits a crystalline product to be deposited continuously and in such a way as to admit of mechanical handling and rapid washing, drying, and sacking, and the most advantageous use of mother liquors.

As an alternative, spray-pond evaporation may be considered, if the loss of water which that involves is not too important an item. Spray-pond cooling is most efficient where the spray maintained is fine, is kept in suspension for a long time (thrown high in the air), and the air circulation is rapid (high winds). Unfortunately, these advantageous conditions entail such great losses through the blowing away of fine spray and desiccated particles that they must be avoided instead of sought. With high winds a coarse spray is the best that can be used. This is sufficient to insure rapid circulation, large surfaces exposed to the evaporating agent, and the prevention of the formation of protective coating of crystals over the surface of the brine. It does not exclude mechanical conveying, washing, drying, and sacking of the crystalline product, though it may not aid in the separation of the sodium and potassium nitrate and the elimination of borax.

The precipitation of impurities should be outside the leaching vats and not within them, both because the latter interferes with further leaching, as has been explained, but more particularly because among the impurities are possible by-products of value. To separate all these by the maintenance and manipulation of equilibria would be quite an undertaking, because, as pointed out by Donnan, one would be led into multiphase systems of great complexity. But in practice such systems may sometimes be greatly simplified through the immediate elimination of undesired components by means other than temperature and volume changes.

More Fertilizer Used on Cotton Acreage

Increased used of fertilizer on the cotton acreage this year as compared with last year is reported to the United States Department of Agriculture. More than 37 per cent of the acreage has been fertilized as compared with 32 per cent last year. A number of individual states show larger gains.

In Georgia the total cotton acreage receiving fertilizer this year was 10 per cent more than last year's acreage. Florida shows an increase of 8 per cent, Alabama 10 per cent, Mississippi 14 per cent, Louisiana 18 per cent, and Arkansas 16 per cent. The remaining cotton states are below the average gain for the belt as a whole.

An average of 260 pounds of fertilizer per acre used is shown for all cotton states, as compared with 251 pounds in 1922. Mississippi and Arkansas show a decrease of 10 pounds per acre and Virginia 15 pounds. In Louisiana the same quantity per acre was used as last year. North Carolina shows the use of 445 pounds of fertilizer per acre as compared with 410 pounds last year; South Carolina, 310 pounds as compared with 280 pounds; Georgia, 250 pounds as compared with 218 pounds; Florida, 250 pounds as compared with 200 pounds; Alabama, 230 pounds as compared with 210 pounds.

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[2] See THIS JOURNAL, **15**, 159 (1923).

The Industrial Outlook for Colloid Chemistry[1]

By Harry N. Holmes

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COLLOID chemistry has already made an important place for itself in the industries, but there are a great number of applications yet to be made. Most plant and animal material is colloidal, consequently the shaping, isolation, and transformation of this material needs the aid of men with a colloidal viewpoint. Even in some minerals and in the clays we find the colloid condition. The study of alloys will probably progress, to some extent, along colloidal lines.

It may be worth while to consider some of the probable colloid industrial developments of the near future.

Plauson's Colloid Mill

This invention of Hermann Plauson, a Russian physical chemist, and Berthold Bloch, a German engineer, is being widely advertised, and its many uses are thoroughly covered by patents before the mills are sold to the public. If it lives up to one-half the promises made for it, this will greatly extend the application of colloid chemistry to the industries.

Two types of mill are made, one a friction machine for more massive material and the other a high-speed impact machine. Plauson speaks of peripheral velocities of 200 meters per second, corresponding to 12,000 revolutions per minute. Even at 40 meters per second he breaks material into particles that remain suspended in suitable liquids. The material to be disintegrated is mixed with a nonconducting liquid and fed into the mill. Because of their coagulating action in the presence of traces of moisture, electrolytes are often excluded. In fact a "disperser" is generally added to nullify their effect. This disperser may be a protective colloid, but sodium hydroxide or ammonia are generally used.

Plauson proposes to disintegrate oil shale in the presence of water so that the oil emulsifies in the water. The emulsion is removed and broken after settling of the sludge. He makes *blanc fixe* by mere pulverizing of barytes instead of by precipitation methods.

Cellulose will be disintegrated into a product of such enormously increased surface that it is attacked by reagents at a velocity not known at present. Viscose silk will be made more readily. Cellulose will be saccharified and converted into alcohol with increased ease. Rubber manufacturers will get finer particles of all material and a better mix. Paint makers will have an additional means of varying the tint and covering power of pigments.

In order to concentrate his product Plauson invented an ultrafilter. With this he also expects to dehydrate clays and to extract oil from oil seeds.

Adsorbent Gels

The recent successful development of gas mask charcoals did much to attract attention to the possibilities of adsorbent gels. These products as used are not jelly-like at all, but hard, and, in some cases, almost glassy in feel and appearance. But since they are dried gels the name sticks. The best known so far is Patrick's silica gel, although several others have been made. Silica gel is easily prepared by adding hydrochloric acid to water glass. A firm jelly or gel soon sets. This is broken into lumps, washed, and dried. After "activating," or heating to about 150° C., it is ready for use. This activation drives off water with resultant formation of a vast number of minute capillaries. The diameter of such a capillary is probably only a small multiple of the diameter of a molecule. It is this vast internal surface that makes such a gel a powerful gas adsorbent.

Silica gel can take up water about as well as does concentrated sulfuric acid; hence, it can be used in drying the air fed into a blast furnace. On moderate heating the gel is regenerated. Since the Gayley dry blast is said to increase the output of a furnace 10 per cent and save 10 per cent of the coke, it is evident that there is a great possibility for the gel in this respect alone.

This same water-adsorbing power points to a large use in vacuum ice plants. By adsorption of water vapor enough cooling is produced to freeze part of the water.

Gasoline may be preferentially adsorbed from natural gas or from still mixtures and released again on moderate heating. The recovery of benzene from by-product gases is of the same order. Oxides of nitrogen may be recovered from all nitration processes and in the manufacture of nitric acid itself. Loss of the catalytic oxides of nitrogen in the lead chamber process may be prevented by the use of silica gel.

A vast amount of sulfur dioxide is wasted in various industries as dilute gas (1 to 4 per cent SO_2). By adsorbing this gas in a gel it may be delivered again in any concentration. This facilitates the manufacture of liquid sulfur dioxide, which in turn is used in sulfite pulp manufacture, refrigerating plants, etc. Lead chamber plants usually operate on 8 per cent sulfur dioxide. With higher concentrations delivered from a gel a greater working efficiency per cubic foot could be secured.

But such gels do more than adsorb certain gases. They adsorb material from liquids. For example, silica gel removes sulfur compounds from crude petroleum or from any of its fractions.

> The formation of gums and resins in gasoline, the poor burning quality of kerosenes containing, in addition to sulfur, a large percentage of unsaturated hydrocarbons, the sludges deposited in lubricating oils, and finally, the discoloration of wax on exposure to light, are all directly due to the presence of sulfur.

Concentrated sulfuric acid has serious limitations as a refining agent, for not only does it fail to remove all the objectionable sulfur compounds, but it does remove unsaturated hydrocarbons of considerable value to gasoline.

These inert silica gels serve as excellent supports for catalysts because of the enormous surface offered.

Sulfite Pulp Waste

About one-half the weight of wood is lignin, and in the separation of cellulose from wood for paper pulp all this lignin is wasted. The concentrated sulfite pulp liquor is a powerful adhesive after drying to a hard solid, yet it softens and disintegrates in the presence of moisture. If it could be made waterproof *after* drying, this liquor would be of enormous value as a cheap road-binder, in making smokeless briquets from hard-coal dust, in roofing preparations, and as an adhesive in making fiber containers.

Syneresis

By "syneresis" is meant the separation of a liquid from a gel after standing some time. This is a very common phenomenon and we need to know more about its control. Lubricating greases "break" or separate free oil from the soap-oil gel after a time. A small amount of water is emulsified in these greases in order to check this undesirable syneresis. The staling of bread has

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[1] Received March 16, 1923. Presented before the Division of Industrial and Engineering Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

been blamed on syneresis with quick evaporation following. Since nearly 10 per cent of all bread baked commercially goes stale, the loss is very great. Katz offers another explanation for the change in bread, but whatever the theory advanced, it seems to be a colloid problem.

SMOKE SETTLING

Bancroft's suggestion that a smoky fog over London or Pittsburgh might be settled by blowing electrified sand from an airplane is arousing much interest. To carry the suggestion further, why not send up (or down, as convenient) a counter smoke or fog with particles of an electric charge opposite to that on the objectionable fog? Mutual precipitation might result, as Gibbs has indicated. Bancroft's device may have an important use in causing rainfall under favorable conditions.

EMULSIONS

The use of gum dammar in making emulsions of the water-in-oil type has recently been patented.[2] Hitherto, heavy-metal soaps and lanolin have been used for this purpose, but there are distinct advantages in the use of gum dammar. By its aid printer's ink as well as lithograph ink may be heavily diluted with water without loss of essential properties. Screens for color photography may easily be prepared by use of this gum in dispersing dyed drops of gelatin water throughout a volatile solvent. In general, any substance soluble in water, glycerol, or alcohol may be dispersed as an emulsion in various fatty and hydrocarbon oils. It is enough if a material be wet by the water more readily than by the oil.

There are many problems of an emulsion nature yet to be solved. As Clayton suggests, we need a centrifugal emulsifier that will remove the emulsified drops as fast as dispersed. The increase in viscosity with increasing richness of an emulsion interferes with free splashing and smashing of drops to be broken down.

Perhaps in its earlier stages an emulsion may best be prepared by shaking or beating, but when it becomes too viscous for easy agitation it should be ground in some sort of a mortar device.

Clayton suggests that the amount of free air in a splash bottle has an influence on the effect due to changing the speed of shaking. The emulsifying agent, always colloidal, may be adsorbed at the surface of each air bubble and thus introduce complications. It is probable, also, that with increasing additions of oil and increasing viscosity of emulsion the speed of agitation should change. Perhaps the time of agitation after each successive addition should change.

There is room for research in breaking emulsions. The water-in-oil emulsions of some petroleums carrying asphaltic bodies have been obstinate. Since they carry as high as 40 per cent water the situation is serious. Electric precipitation of water drops has been fairly successful. Addition of a hydrophile colloid that would disperse in the water drops and so offer a counter emulsifying effect opposing that of the asphalt in the oil, has been tried with good results on some oils. Phenol, soluble in both oil and water, has been used to carry hydrogen ions into the water drops, thus neutralizing the negative charge on the drops.

WETTING POWER

The ability of a liquid to spread over a solid is measured as "wetting power." It is influenced by low surface tension of the liquid, by high superficial viscosity of the liquid, and by adsorption of the liquid at the solid surface. Wetting power may be measured by the contact angle between liquid and solid and a device for such accurate measurement is now on the market.

Since wetting power is of great importance in emulsification, flotation of minerals, lubrication, application of sprays and dips to plants and animals, it is obvious that there is work worth doing in this field. Coal dust may be separated from slate by utilizing the fact that coal is more readily wet by oil than by water while the opposite is true of slate particles. This is the principle that enables us to concentrate sulfide ores (and some others) by flotation in an oily froth. Why not study the flotation, by preferential wetting, of factory dust? A cheap salvage of particles of value is possible.

Chick and Martin[3] believe that with coal-tar disinfectants the bacteria are adsorbed on the emulsified particles of the tar acid, thus being brought into contact with disinfectant in a most concentrated form. A poisonous dip for cattle was given increased wetting power, thus permitting its sodium arsenite content to be lowered to a point not injurious to cattle. By this means the cattle tick was conquered over wide areas.

LUBRICATION

"Oiliness" is a term now much used to name the property of maintaining a film of lubricant between shaft and bearing. This property depends to some extent on surface tension and viscosity, but is also greatly influenced by the adsorption of the lubricant on the metal bearing surfaces. Obviously, a change in the bearing changes the extent or intensity of adsorption.

Heavy mineral oils, according to Dunstan and Thole,[4] are probably iso-colloids—that is, polyphase systems in which the dispersed component is of the same chemical nature as the dispersion medium.

These larger molecular aggregates of the oil by lowering surface tension should concentrate at the oil-metal interface. Doubtless, this film is the actual lubricant. Dunstan and Thole believe that certain unsaturated constituents of oils promote oiliness by forming a physico-chemical union with the bearing surface. Stanton, Archbutt, and Southcombe[5] recently announced that by adding 1 per cent of free fatty acid to a mineral oil they decreased friction as much as by the presence of 60 per cent of pure rape oil.

In general, we must learn exactly what constituents of fatty oils and mineral oils give the greatest lubricating effect. Possibly we may synthesize new products that may be colloidally dispersed in some neutral liquid and be powerfully adsorbed by bearing surfaces to form the proper sort of films.

The Deeley friction machine and the Lanchester oil gear-testing machine are now available—at a high price. Bingham[6] proposes to measure oiliness by use of an inclined plane device and by the use of a lubricant as a cutting oil.

CARBON BLACK AND LAMPBLACK

When natural gas is burned with insufficient air, the smoky flame yields carbon black on chilling with a metal surface. Similar combustion of oils, pitches, and tars yields lampblack, an inferior product. Carbon black is essential as the pigment in printer's ink and as a filler for rubber tires. When natural gas is exhausted we shall have the problem of making an adequate substitute for carbon black. Lampblack particles are covered with a film of tarry material, so it is proposed that such carbon particles be chilled at a temperature too high for condensation of oily or tarry matter. This is a step in the right direction. Carbon black particles are the smallest of all such blacks.

GLASS AND ENAMEL

Since ions exist in melted salts, there is a possibility that certain ions in melted glass or enamel may peptize (subdivide or protect) a pigment added to the melt. Coagulation by ions may also merit study in such systems. The composition of enamels might be changed so as to introduce desirable ions or even protective colloid material.

PAPER AND PAINTS

When uniform spherical particles are closely packed, each one touching twelve others, they occupy about 74 per cent of the total volume. Yet smaller spheres may be added to occupy part of the 26 per cent of voids. Still smaller ones added to these will further help to fill voids. Why not apply this principle in making a thin paper more opaque? If different sizes of appropriately graded clay filler were added, more clay could be carried in a given volume, thus making a denser paper. Of course, any clay filler is made up of mixed sizes, but some study of the most effective differences in size should be worth while. The same reasoning applies to the manufacture of a paint of maximum hiding power.

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[2] U. S. Patent 1,429,430 (September 19, 1922).

[3] *J. Hyg.*, **8**, 698 (1914).

[4] *J. Inst. Petroleum Tech.*, **4**, 191 (1918).

[5] *Engineering*, **108**, 758 (1919).

[6] *Bur. Standards, Tech. Paper* **204** (1922).

Many other possible developments of industry along colloidal lines could be mentioned. A factory waste suspended in water might be precipitated by formation of countless minute air bubbles. Adsorption films should form at the bubble-water interface. Added salts might aid this partial coagulation. The de-inking of old newspapers (7000 tons wasted daily) by loosening the carbon black with dilute alkali and then adsorbing the carbon on a colloidal clay such as bentonite, which carries the black right through a paper filter, is an assured success, according to the United States Forest Products Laboratory. Saklatwalla[8] proposes adsorption of gases on metals as a criterion of corrosion. He notes the fact that the metals least corroded—such as platinum, palladium, and tungsten—are the ones that can adsorb large volumes of gases.

Fundamental properties of colloidal systems must be studied first. Applications will follow readily enough. Colloid fellowships would greatly aid in increasing our knowledge of these fundamentals and also serve to train men who could apply these principles to the industries. Such fellowships could be supported by a single company interested in contributing its share to the common fund of knowledge, or by a group of industries.

[8] *Chem. Met. Eng.*, **27**, 647 (1922).

Safety and Efficiency in the Chemical Industry[1]

By L. A. DeBlois[2]

E. I. du Pont de Nemours & Co., Wilmington, Del.

BEFORE attempting to establish the relation of safety to efficiency in any industry, or in industry as a whole, we must define the terms and compare the basis of measurement. The occurrence of accidents, either their number (frequency) or their extent (severity), is the index, not of safety, but of its reciprocal, the hazard. The basis of measurement is exposure, expressed either as man-hours (payroll-hours) or, where the number of hours of exposure per day is practically constant or where a statistical day is assumed, simply as *men*. The precise form in which the basis is applied is immaterial—what we should keep in mind is that it expresses human exposure to accident.

Relation between Safety and Efficiency

The index of efficiency in the engineering sense is output, and the base, input, both being expressed in the same units. In industry these units are always material—so many thousand bottles, or so many tons of castings—but never so many thousand human beings, or so many thousand payroll-hours. Obviously, then, we cannot directly compare safety and efficiency, since we do not measure them by the same yardstick. We do, however, express output as so much production per man, and this we may compare with accident occurrence since both are calculated on the basis of exposure (man-hours).

We all know that output depends upon the mental and physical equipment of the individual worker, the mechanical equipment furnished him for doing his work, upon the condition of these three forms of equipment, and upon the skill and energy with which he employs them. So also with accident prevention—it depends upon mental, physical, and mechanical equipment, and upon the degree to which it is successfully applied by the individual. The degree to which any given equipment is successfully applied to its purpose is in a general sense its efficiency, and so we may write down that both output and safety depend upon the mental and physical efficiency of the worker and upon the mechanical efficiency of his working equipment. If we increase any one of these we shall expect to find a simultaneous increase in output and safety, provided that which we term "efficiency" is in each case true efficiency.

As illustration let us consider the handling of acid in carboys in comparison with the use of tank cars. The carboy method is mechanically less efficient because of higher acid losses. These arise principally from (*a*) overflow or leakage while filling, (*b*) breakage or leakage in transportation, (*c*) leakage or loss while emptying, (*d*) acid residue after emptying. There are also evaporation losses which are probably not material with proper stoppering.

With tank cars there are corresponding possibilities of loss, but if the equipment is given inspection and repair commensurate with the value of the container and its contents, the total losses per unit of acid handled are actually less.

In the matter of injury occurrence, the use of carboys is much more hazardous than the use of tank cars. Men are apt to be burned if carboys overflow while filling, or if they break, or if they are emptied carelessly, or if they contain a small amount of acid when thought to be empty. It is true, if a tank car starts a leak its entire contents may be lost, but such leaks are infinitely less frequent than instances of carboys breaking, and after all it is generally the first contact with acid rather than the total amount of acid liberated that is associated with the injury. However this may be, the interesting point is that the mechanical conditions which cause losses and lower the mechanical efficiency of the process are exactly the same conditions which cause injuries to the workers.

Extra Hazards in Chemical Industry

Each material handled in industry has its own potentiality for causing accidents—heavy materials crush by their weight, sharp materials cut or abrase, hot materials burn or scald—but in the chemical industry we encounter materials with additional properties—for example, materials such as acids and caustics which, though cold, cause burns; materials which give off corrosive, suffocating, or toxic vapors; materials which poison through the unbroken skin; materials subject to sudden and perhaps violent decomposition, etc. So also with the processes in which the materials are employed; they have the common mechanical hazards inherent to a mechanical process plus additional hazards introduced by the presence of materials with extrahazardous characteristics. By way of illustration, we may think of a workman whose eye is struck by a particle thrown from the basket of a centrifugal wringer. Ordinarily, the result is a slight abrasion of the cornea, but if the particle is caustic the abrasion is complicated by a caustic burn. One readily sees, then, that the accident hazards of the chemical industry should be intrinsically greater than those of general industry.

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[2] Manager, Safety Division, Service Department.

It is natural that the chemical industry should have acquired the reputation of being inherently hazardous, and we will grant that accidents at many chemical plants have been frequent and often severe, and that the materials themselves and therefore the processes in which they are involved may be more hazardous than other corresponding industrial processes not employing hazardous materials. This may be the case, however, without the industry itself or any typical plant of the industry being "inherently" hazardous in the sense that the extra hazards cannot be obviated.

We have already seen that safety is dependent, not alone on mechanical efficiency, but upon mental and physical efficiency as well, and in the well-regulated chemical plant a wholesome respect for the accident-causing properties of the materials being handled may quite offset the extra hazards of the materials themselves—in other words, the greater material hazards are balanced by higher mental and physical efficiency in the organization. To accomplish this employees need not be necessarily higher paid or of higher mental caliber, but they must at least be carefully instructed in the hazards of the processes as well as in their regular duties. Furthermore, they must be carefully supervised in their work. The motto of a chemical plant must be literally "Safety First," not set forth as a mere bulletin board slogan, but as a working precept in which the plant management devoutly believes. When such question arises safety must actually take precedence over production and quality, for if safety is sacrificed both production efficiency and quality efficiency will suffer. No plant manager need fear to enunciate the principle of "Safety First."

COMPARISON OF ACCIDENT RECORDS OF CHEMICAL AND NONCHEMICAL OPERATIONS

E. I. du Pont de Nemours & Company has chemical plants manufacturing high explosives, smokeless powder, acids, charcoal, dyestuffs, certain cellulose products, and chemical laboratories, etc. It also has what might be termed "nonchemical operations," including plants manufacturing paints, other cellulose products, blasting caps, boxes, shooks, etc., and also miscellaneous construction work. (The manufacture of black powder, a mechanical operation with chemical hazards, is in an anomalous class and has been excluded.) For the year 1922 the relative accident records of these two groups were as follows:

	Chemical	Nonchemical
Payroll force	3269	4700
Injury frequency rate	29	34
Lost time rate	0.52	1.09

In this comparison there is nothing to suggest the presence of a preponderant chemical hazard, and on a well-established, well-ordered plant one generally finds that the process men as a group are as well able to maintain a long record without injury as the mechanical group. In fact, the most frequent general cause of injury in any group is handling of objects such as boxes, barrels, or other containers by hand.

The foregoing relates to frequency of accidents and lost time from accidents. Lost time, however, is not a true measure of severity, but must be weighted for mutilations (permanent disability cases) and death. If such basis of comparison is used we find that chemical plants rate higher than nonchemical plants, owing to the more frequent occurrence of serious injuries and fatalities in the former. The extreme condition is probably encountered in explosive manufacture, where a relative trivial occurrence that would under ordinary conditions cause only a slight injury, or even no injury at all, leads to an explosion and death.

EFFECT OF EMERGENCY METHODS

It has been pointed out that accident frequency is low in a well-established chemical plant. It is unfortunate, however, that many chemical plants cannot be termed "well established," because processes are constantly being altered and more or less temporary or makeshift equipment is in daily use. Furthermore, there constantly arises the necessity of employing what might be called "emergency methods"—methods not followed in regular and standardized operating practice, but evolved on the spur of the moment either after breakdown or other stoppage of operations through unforeseen circumstances or upon starting up a new operation. In the Dye Works of the du Pont Company during 1922, sixty per cent of the injury severity rate was due to such emergency methods. For its interest in this connection the following is quoted from instructions sent out by the Works Safety Committee:

> The use of "emergency methods" is at present unavoidable and this Committee, recognizing this fact, desires to secure your coöperation in minimizing the dangers of their employment. In view of the fact that these methods are evolved under stress, the Committee wishes that checks of the following nature be considered:
>
> (1) Responsibility for use of emergency methods be clearly placed on supervisors and foremen—i. e., use of these methods must have their O. K.
>
> (2) Someone in a supervisory capacity should be present until difficulties have been overcome and operation is moving normally or has been shut down safely.
>
> (3) Great care should be taken to thoroughly protect, by means of goggles, gloves, etc., all men working under emergency conditions.

One reads in such injunctions the result of close scrutiny of working conditions and an evident indication of practical rather than emotional efforts to prevent accidents.

NEED OF PLANT DISCIPLINE

Discipline in a chemical plant must be strictly maintained, for in no other industry is there greater possibility of injury to others and destruction of property through the thoughtless act of a careless man. The first and indispensable step towards proper discipline is a careful investigation of every accident, major or minor. We hesitate to use the expression "fixing the responsibility," but the extent of the responsibility of the individual, the foreman, the superintendent, and the management must be determined, not on the basis of actual results, but upon the basis of what might readily have happened. It is generally stated that 75 to 80 per cent of accidents are caused by the carelessness or ignorance of the employee. This is open to question. It is probably true that 75 to 80 per cent might have been prevented by greater care or by display of greater intelligence on the part of the employee, but many might also have been prevented by foresight and action on the part of the foreman, the superintendent, or the management. In fact, accidents for which the responsibility is single are the exception rather than the rule. Humanly, the blame is generally placed "on the other fellow."

In this connection the following assignment of responsibility for du Pont Company injuries in 1921 is of interest:

	On Basis of —			
	Frequency %		Severity %	
Unavoidable:				
Unknown physical deficiency	2.6		0.8	
Risk of employment	23.0		43.8	
TOTAL		25.6		44.6
Fault of employer:				
Defective construction or equipment	16.0		3.9	
Lack of proper safety appliances	4.8		19.1	
Lack of proper supervision	10.9		10.4	
TOTAL		31.7		33.4
Fault of injured:				
Negligence or lack of skill	29.9		12.5	
Disobedience	3.9		0.5	
Failure to use safety appliances	1.4		0.4	
Failure to report injury	3.4		8.0	
TOTAL		38.6		21.4
Fault of fellow-employee:				
Negligence or lack of skill	3.5		0.6	
Disobedience	0.6		0.0	
TOTAL		4.1		0.6
		100.0		100.0

This tabulation is a frank statement of findings, and definitely contraverts the loose statement that the majority of injuries are caused by the negligence or ignorance of the man injured. One wonders what would be shown in a similar tabulation of the experience of a large corporation which had not consistently expended money and effort in accident prevention.

Next in importance to proper discipline is the careful selection, assignment, and instruction of new employees. Du Pont Company experience shows that the accident-frequency rate for employees of less than one month's service is twice that of employees of one year's service or over. If there are special hazards from toxic materials, new employees should be physically examined, graded, and assigned only to employment to which they are suited. At the Dye Works, for example, accepted applicants are physically graded into three active classes and a fourth class to which employees are assigned for light work only. Employees of the first two classes are physically examined each month. The various operations are also graded into four corresponding classes. The first class involves exposure to nitro and amido bodies; in the second class, these bodies are present but direct contact with them is unlikely; in the third class, such bodies are absent or contact with them is practically impossible; the fourth class covers miscellaneous light work. No employee of one class is permitted to work in a process of a more hazardous class, this restriction applying also to mechanical and labor department employees, who are graded in the same manner as the process workers.

Much might be written of other essentials of a safe chemical plant, the least of which is by no means scrupulous cleanliness in mechanical, structural, and human equipment. The same outstanding deduction, however, is to be drawn in every case—that what reduces accidents makes also for increased efficiency. It is sometimes difficult to show in book values the profits that accrue from organized safety work, properly conceived and conscientiously carried out, because such profits, though real, are often intangible. On the other hand, no one will gainsay the economy of "efficiency," and if safety and efficiency go hand in hand, what greater encouragement to prevent accidents should we demand?

Recent Important Investigations in the Chemistry of Rubber, and Substantiation of the C_5H_8 Ratio[1]

By Harry L. Fisher

THE B. F. GOODRICH CO., AKRON, OHIO

A review has been given of the more important recent investigations on the chemistry of rubber showing the following results:

(1) Substantiation of the C_5H_8 ratio and the C_5H_8 nucleus as the fundamental grouping in the rubber hydrocarbon, and the presence of a double bond for each C_5H_8 nucleus.

(2) Hydrogenation of rubber directly and in solution has been accomplished.

(3) Studies in oxidation have produced new products, especially $(C_5H_8O)_x$.

(4) Viscosity measurements have shown that the change during the heating of a solution of rubber is reversible, provided air is excluded.

(5) Concentrated sulfuric acid on a rubber solution produces what appears to be an isomerized rubber.

NOT since the publication of Harries' work on the ozonides and hydrohalides of rubber a decade ago has so important a paper on the chemistry of rubber come forth as that by Pummerer and Burkard.[2] These chemists have accomplished the "impossible"—they have hydrogenated rubber at ordinary temperatures. Furthermore, by extremely careful work they have substantiated by analysis that the empirical formula of the rubber hydrocarbon *is* C_5H_8, and by their method of hydrogenation that each C_5H_8 nucleus *does* contain a "double" bond.

THE C_5H_8 RATIO

It is interesting that their paper should come out at the same time that serious questions were being raised concerning the empirical formula of rubber. Kirchhof[3] has given much time in reviewing the work of many authors, including himself, in an effort to show that the empirical formula is $C_{10}H_{17}$ (instead of $C_{10}H_{16}$, which is the same ratio as C_5H_8), and indeed the array of evidence is considerable. However, he presents the figures only and does not at the same time compare the methods of preparation of the samples for analysis. Pummerer and Burkard were unusually careful in this regard. They recognized the ease of oxidation of pure rubber and how readily a small amount of oxidation which will vitiate an analysis can occur. Therefore, although they used Harries' procedure in general, they protected the rubber all the time by keeping it in an atmosphere of carbon dioxide. The results of their analyses are so good and so important that it seems worth while to give them here. Harries' best result is also given for the sake of comparison.

	C		H	
Calculated		88.15		11.85
Pummerer and Burkard . . . . Found	87.99 87.99 87.89	87.96	11.79 11.85 11.81	11.82
Harries[4] .... Found		87.85		12.28

PRESENCE OF DOUBLE BONDS SHOWN BY ADDITION OF HYDROGEN

The other serious question settled by Pummerer and Burkard is the nature of the unsaturation. Recently, Boswell[5] has proposed a new structural formula for rubber largely on the basis of its containing no double bonds. His argument is as follows:

> With double bonds existing in the rubber molecule, it should be possible to add hydrogen directly and produce a saturated hydrocarbon. The endeavors of Harries and of Hinrichsen and Kempf to accomplish this failed. Likewise, all attempts made in this laboratory were unsuccessful. This would seem to indicate that rubber contains no ethylene linkages at all. Belief in the unsaturated character of rubber depends on the observations that rubber adds on approximately four bromines and two hydrochloric acid mols for each $C_{10}H_{16}$. However, as these are admittedly very drastic actions, almost certainly accompanied by deep-seated depolymerization of the rubber molecule, it is conceivable that the rubber mol itself contains no double bonds

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[1] Received February 23, 1923. Presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Ber.*, **55**, 3458 (1922); *C. A.*, **17**, 898 (1923).

[3] *Kolloidchem. Beihefte*, **16**, 47 (1922); *C. A.*, **16**, 4363 (1922).

[4] "Untersuchungen über die natürlichen und künstlichen Kautschukarten," p. 7.

[5] *Can. Chem. Met.*, **6**, 237 (1922), *India Rubber J.*, **64**, 981 (1922).

whatever, and that these are only produced by the breaking up of the complex rubber molecule by the action of bromine or hydrochloric acid. That bromine and hydrochloric acid add to a polymerized compound like rubber constitutes no proof that ethylene linkages are present in the original rubber molecule.

Pummerer and Burkard give a series of fifteen experiments very successfully demonstrating that at the ordinary temperature in the presence of a catalyst rubber adds two atoms of hydrogen for each C_5H_8 nucleus. The purified rubber was dissolved in either hexane or hexahydrotoluene, and a concentration of less than 1 per cent had to be used in order to obtain a complete reaction, 0.2 to 0.6 per cent being the best. Higher concentrations would not work well, possibly, according to the authors, because of the inactivation of the catalyst by absorption of rubber. The catalyst was platinum black activated by oxygen according to the method of Willstätter and Waldschmidt-Leitz.[6] The total time necessary for the complete absorption of the gas varied from 3 to 170 hours, the shorter time usually at temperatures of 70° to 80° C. The agreement with the theory by volume measurements was exact in one case and generally not more than 1 per cent off—that is, not more than 2 cc. in approximately 200 cc. of gas absorbed. These figures were checked by the actual isolation of the hydro-rubber and analysis by combustion. The hydro-rubber is similar to rubber itself in that it is highly elastic, but it is almost colorless and is soluble in ether, giving a colloidal solution. It is extremely susceptible to air oxidation, especially in the presence of the catalyst. Oxygen transforms it into a substance with the same empirical formula as natural rubber. This new rubber is not the same as natural rubber and is called iso-rubber H. It is soluble in ether, and, like rubber, on hydrogenation adds two atoms of hydrogen for each C_5H_8 nucleus. This new hydrogenated rubber is also readily oxidized, but it has not been investigated further.

The authors are aware of the fact that the ease of oxidation of the hydro-rubber brings up the question as to whether the hydrogen atoms are bound by primary valences. They state that the stability of the substance in a high vacuum (1 mm.) argues against a secondary valence combination with the colloid. To the writer this unusual reaction—oxidation resulting in the formation of an unsaturated compound—recalls the unique case of 1,2-dihydrobenzene, which, even though it contains two double bonds, will on mild oxidation go over to benzene, a stable though in some respects more highly unsaturated system.

Pummerer and Burkard give the equation for the addition of hydrogen as follows:

$$(C_5H_8)_x + xH_2 = (C_5H_{10})_x$$

where x is the number of isoprene residues in the rubber molecule. Moreover, an equally long open chain must take up one mol more of hydrogen—i. e., $x + 1$ mols, or:

$$(C_5H_8)_x + (x + 1)H_2 = C_{5x}H_{10x+2}$$

It is readily seen that the number of mols of hydrogen consumed in the case of the open chain is $\frac{1}{x}$ times greater than the corresponding number of isoprene groups of the ring system. Now, the authors are certain that a difference of as much as 10 cc. in excess could and would have been detected in their apparatus. If the difference were as great as this it would correspond to a value of 20 for x, where the volume absorbed was about 200 cc., as it was in several of their best experiments. The actual excess was never greater than 2 cc. They therefore feel that they have proved that the rubber molecule must contain a ring system or an extremely long chain in which $x > 20$.

STAUDINGER AND FRITSCHI'S METHOD OF HYDROGENATION

Staudinger and Fritschi,[7] working independently of Pummerer and Burkard, reported at almost the same time that they had succeeded in completely hydrogenating rubber. Their paper was actually published a month earlier.[8] Their method also comprised the use of a catalyst, but they found it necessary to use very high temperatures and pressures. They employed ordinary platinum black, which was incorporated into purified rubber by mixing it with the benzene solution, then precipitating with alcohol and drying in "absolute vacuum." This platinized rubber without any solvent was placed in a glass container in a rotating autoclave filled with hydrogen at 93 atmospheres and heated for 10 hours at 270° C. or at 102 atmospheres and 280° C. Lower temperatures gave no or only partial hydrogenation. At ordinary pressure but the same high temperature only partial hydrogenation was effected after 7 days while hydrogen was passing all the time. Nickel works much like platinum, but not so rapidly and completely. The hydro-rubber is a colorless, transparent, tough mass entirely without the elastic properties of rubber. The loss in color is said to be very characteristic of the reaction. The analyses check the empirical formula, $(C_5H_{10})_x$, very closely. The authors state that according to the properties of the hydro-rubber it can be considered as a saturated hydrocarbon with so great a molecular weight that, so far as can be shown by analysis, no distinction can be made between $C_{5x}H_{10x}$ and $C_{5x}H_{10x+2}$. The product is soluble in benzene, chloroform, and ether, and insoluble in alcohol and acetone. Its solutions are colloidal and in benzene showed no depression of the freezing point. Its solutions do not decolorize bromine solution, but on standing in the sunlight a substitution product is formed with the evolution of hydrogen bromide. The hydro-rubber is unattacked by sulfur monochloride in solution, being recovered unchanged. It is therefore very stable toward chemical reagents, as would be expected from a saturated ring or straight-chain hydrocarbon of high molecular weight. The authors apparently did not find it necessary to guard against oxidation or they would have mentioned it. Their hydro-rubber is evidently quite different from the hydro-rubber obtained by Pummerer and Burkard.

Staudinger and Fritschi wished to avoid using the large amount of solvents necessary for purification of crude rubber according to the method of Harries. They found Wildermann's method[9] excellent. It consists in extracting the crude rubber with a mixture of two solvents, of which one dissolves rubber and some of the resins, the other dissolves the resins and precipitates the rubber. This allows a more thorough extraction of the resins. Mixtures of chloroform and acetone, 20 to 80 up to 40 to 60 parts, were used for the extraction lasting 8 to 14 days. During this time air was not permitted to enter the apparatus, in order to avoid autoxidation. The authors make the significant statement that although nitrogen was of course present in the crude rubber, only traces or none at all could be detected in the purified rubber.

HEAT DECOMPOSITION

Staudinger and Fritschi thoroughly reinvestigated the heat decomposition of purified rubber in a vacuum of 0.1 to 0.3 mm. pressure. The final temperature of the metal bath was 350° C., but the temperature of the distilling vapors rose only to 320° C. 36.5 per cent remained as a resinous mass which was found to be only about one half as unsaturated as rubber. Fractionation of the distillate in a high vacuum, determination of the boiling point, molecular weight, refractive index, bromine absorption, etc., of the chief constituents showed the presence of isoprene, 3.1 per cent; dipentene, 8.8 per cent; a $C_{15}H_{24}$ hydrocarbon with two double bonds and two rings, possibly a hydronaphthalene derivative, 4.4 per cent; $C_{20}H_{32}$ containing three double bonds and two rings; and $C_{25}H_{40}$ containing four double bonds and two rings. No open-chain terpenes were found.

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[6] *Ber.*, **54,** 122 (1921).

[7] *Helv. Chim. Acta*, **5,** 785 (1922); *J. Chem. Soc.* (*London*), **122,** 1043 (1922); *J. Soc. Chem. Ind.*, **41,** 868A (1922).

[8] Pummerer and Burkard, however, presented their paper at the Centenary of German Scientists and Physicians, Leipzig, September 17 to 24, 1922, and an abstract of their paper appeared in *Chem. Ztg.*, **46,** 883 (1922).

[9] D. R. P. 229,386; *C. A.*, **5,** 2439 (1911).

Staudinger believes that the splitting of the carbon atoms takes place in the 1,4 position, or in multiples thereof, like 1,8; 1,16; etc. This is also in accord with his earlier work[10] on the heat decomposition of dipentene into isoprene, in which there was the same type of splitting. This experimental evidence is against Boswell's contention that the splitting should take place at the double bonds. It is true that the double bonds are "usual points of weakness," but that condition is in connection with the action of chemical reagents and not necessarily of heat.

The hydro-rubber was subjected to a similar heat decomposition. While the rubber was practically completely decomposed at 300° C., it was necessary to raise the temperature of the metal bath to 350° C., and finally to 400 C. in order to complete the decomposition of the hydro-rubber. Only about 0.6 per cent remained behind. The distillate contained products entirely different from those from rubber, most of them apparently being straight-chain compounds containing one double bond each, such as pentene, C_5H_{10}, a $C_{15}H_{30}$ compound, $C_{45}H_{90}$, and $C_{50}H_{100}$.

HARRIES' α HYDRO RUBBER

In an inaccessible journal[11] Harries and Evers have described the preparation of a partially hydrogenated rubber by the removal of the chlorine from the "dihydrochloride" of rubber with zinc in ethylene chloride solution in the presence of hydrogen chloride. The analyses vary but the best agree with the formula $(C_{10}H_{18})_x$. The substance has the general appearance and some of the properties of gutta-percha, forms colloidal solutions, and is unsaturated. It forms an ozonide which is nonexplosive and on hydrolysis gives no levulinic aldehyde. Furthermore, heat decomposition of the α-hydro-rubber at a low pressure gives no isoprene.

OXIDATION

Pummerer and Burkard found that very dilute solutions of pure rubber absorbed oxygen gas at room temperature, the amount corresponding to 0.5 mol of oxygen for each isoprene residue agreeing with the formula $(C_5H_8O)_x$. The result was the same with or without platinum black and the absorption was complete in 40 to 50 hours. The product was not isolated. They also found that perbenzoic acid, $C_6H_5CO.OOH$, reacted normally toward rubber, in chloroform solution, in absence of moisture, one mol being used for each C_5H_8 nucleus. This reaction was followed by titration of the reagent and verified by the isolation of the rubber oxide formed. It is a white, tough substance, much less elastic than rubber, and insoluble in all the ordinary solvents. Their analysis shows that it has the empirical formula $(C_5H_8O)_x$:

	C Per cent	H Per cent
Calculated	70.83	9.53
Found	70.70	9.77

This is believed to be a new oxide of rubber and, like the hydro-rubber, shows again that the fundamental grouping in the rubber molecule is C_5H_8, and not $C_{10}H_{16}$, as was assumed for many years.

Boswell[5] and his students have carried out some interesting work on oxidation with potassium permanganate, hydrogen peroxide, air, and a mixture of hydrogen peroxide and iodine. The analyses of the products correspond, respectively, in general to the empirical formulas: $C_{25}H_{40}O$, $C_{25}H_{40}O_2$, $C_{10}H_{16}O$, and $C_{25}H_{40}IO_8$. The substances are mostly resin-like. The author starts with $C_{30}H_{48}$ and gives hypothetical structural formulas for rubber and all these oxidation products.

VISCOSITY

Considerable work has been done on the viscosity of rubber solutions, especially in studying the effect of heat. Harries[12] tells of the marked falling off in viscosity when a solution is boiled for a long time and then cooled, and accounts for the change on the ground that depolymerization has taken place. Lichtenberg[13] showed that such solutions may give no precipitate with alcohol and that the action of hydrochloric acid gas gives a hydrochloride which contains less chlorine than that obtained in the same way from the unheated solutions. There is no question as to the change in viscosity on heating, but there has been a question concerning the reversibility of the change. Pummerer and Burkard carried out the heating in the presence of carbon dioxide, also providing against the loss of solvent. Their experiments, involving 8 hours boiling followed by slow and by rapid cooling, indicate that no appreciable change takes place. They also kept rubber solutions protected with carbon dioxide in brown flasks exposed to the sun for several months during the unusually warm summer of 1921, and found that alcohol precipitated the rubber in a normal fashion and that the precipitate was not soluble in ether. Without these precautions Harries had found that alcohol precipitated an oily mass which was soluble in ether.

GEL FORMATION OF RUBBER IN BOILING BENZENE SOLUTION

A 2 per cent rubber solution boiled under protection of carbon dioxide showed no change, but with a 4 per cent solution under similar conditions there occurred a separation of a yellowish gel on the bottom and walls of the flask as soon as the boiling point was reached, according to Pummerer and Burkard. Evaporation of the solvent was guarded against. A 10-hour experiment at 50° C. gave no separation. The gel formation is reversible, since on quick cooling followed by long standing at room temperature it goes back into solution. The amount separated was about 10 per cent.

ACTION OF CONCENTRATED SULFURIC ACID

Kirchhof[14] has studied the action of concentrated sulfuric acid on rubber both in and out of solution. A precipitate is formed in solution which is insoluble in the ordinary solvents and appears to be an isomerized rubber which is less unsaturated than rubber itself. Analysis showed only 0.9 per cent sulfur present. Its specific gravity is 1.094/20°. Kirchhof believes that some of the double bonds have saturated each other, with the formation of tetramethylene rings, and proposes a spiral formula to account for this. On the basis of his work he also proposes a new empirical formula, $(C_{10}H_{17})_x$, for the rubber hydrocarbon in Para rubber,[15] as mentioned above, but the later work of Pummerer and Burkard shows conclusively that his contention is not correct. Rubber on long standing in concentrated sulfuric acid gives oxidation products from which Kirchhof has isolated an acid with the molecular formula $C_{20}H_{30}O_3$.

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[10] Staudinger and Klever, *Ber.*, **44**, 2212 (1911).

[11] *Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern*, I, Zweites Heft, 87 (1921); *C. A.*, **16**, 3232 (1922).

[12] *Loc. cit.*, p. 7.

[13] *Ann.*, **406**, 238 (1914).

[14] *Kolloid Z.*, **30**, 176 (1922); *C. A.*, **16**, 1885 (1922).

[15] Kirchhof states that African rubbers have the usual $C_{10}H_{16}$ ratio.

Heat Transfer Symposium

A symposium on Heat Transfer is being arranged for the 1924 Spring Meeting of the **AMERICAN CHEMICAL SOCIETY**. Those interested are requested to write to the chairman, W. H. McAdams, Massachusetts Institute of Technology, Cambridge, Mass., at their earliest convenience, indicating provisional title where possible. The final manuscript must be in the hands of the chairman by March 1, 1924.

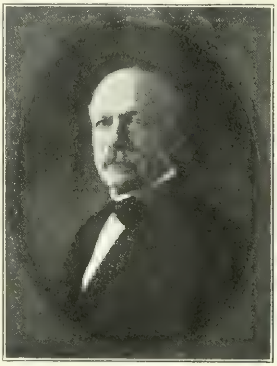
A trust fund for establishing a fellowship in biological chemistry in the College of Physicians and Surgeons, Columbia University, to be named in honor of the founder of that department, William John Gies, will be presented at its twenty-fifth anniversary. The committee will also present to Professor Gies an illuminated book containing testimonial letters of appreciation from former students, and from friends in this country and Europe.

AMERICAN CONTEMPORARIES

Alfred Springer

Although I have known Springer since 1884, he has succeeded in concealing some of his good deeds from me until recently when I have had reason to look them up. We met yearly at the midsummer meetings of the A. A. A. S. He and Wiley and Munroe were leaders of the work and fun. Much of the fun developed in Section Q and was not mentioned in the program. There was a new quantum of stories every year. The membership was not limited to the chemists, and among attendants from other sections I can remember Alvin Clark and Brashear and one-armed Major Powell.

Springer and Wiley were full of mischief all through the meetings. I can recall many pranks they played. Most of these were known only to the élite, who enjoyed them the more. They were pure fun and left no sting. We were few in number and well acquainted. We hailed one another with delight and said good-bye with regret. Evening sessions were few and so there was plenty of time for fun, for we spent a week together. Each one had his pet enthusiasm. Springer had an aluminium violin, equal or superior to any Stradivarius, with which he proceeded to complete our musical discrimination. At another session he lectured to us learnedly on the theory of the balance, and trotted out his own, which was modestly named the "Torsion" balance, and was and is a truly remarkable instrument. On another occasion he told us about fermentation without nitrogen, which anticipated the discoveries of Hellriegel and Wilfarth.


ALFRED SPRINGER

I gathered the impression then, which I have never lost, that his scientific attainments were of the first order. This was also the opinion of a kind lady who listened to his inaugural address as vice president of Section C. She came forward, shook his hand, and said: "Dr. Springer, I did so enjoy your address, it was so simple." He enjoyed telling this story.

John Uri Lloyd tells me that Springer was the man who was most responsible for the birth and subsequent activity of the Cincinnati Chemical Society, a forerunner of the AMERICAN CHEMICAL SOCIETY. The first meeting was held at his house, the second over the drug store of a Mr. Rheum. F. W. Clarke, then at the University of Cincinnati, and later T. H. Norton were also active.

Dr. Springer became a resident of Norwood, five miles from Cincinnati, of which it now forms a part, and has been an active public-spirited citizen, conniving at the establishment of water works, gas works, sewers, and other public utilities.

Wiley says that "Alfred knows more about the essences, ethers, esters, aldehydes, and acids, which are used by the rectifiers to make crooked whisky, than anybody else in the country except myself. His firm has always been manufacturers of complete outfits of artificials for the rectifier. I imagine he is now in cahoot with the bootleggers." Alexander Fries & Brother were his uncles, and he has now become sole proprietor of these large works.

Dr. Springer is of German descent and his daughter married a German naval officer several years before the war began. This placed him in a cruel position, in which he sustained himself to the satisfaction of his friends. Wiley says, further: "I have been with him in all kinds of companies and celebrations; I have heard him speak on hundreds of different subjects, and I never heard him say a mean or disrespectful thing about anybody, not even his intimate friends." Neither have I. He is a credit to his profession and to his race. I feel certain that in this brief sketch many things have been omitted which should be told. They are omitted because they are known only to himself.

EDWARD HART

Honorary Degrees Conferred at Cambridge

At the meeting of the Union Internationale and of the Society of Chemical Industry at Cambridge on Wednesday, June 20, the vice chancellor, preceded by the Mr. Bedells and followed by the university marshal, headed a procession clad in scarlet and other gay colors to the Senate House. Degrees of Doctor of Science (*honoris causa*) were conferred upon seven eminent professors of chemistry with due solemnity. There is a calm dignity about such proceedings which appears to be a survival from a period when trains and telephones did not exist and time was ampler than now. The public orator, Dr. Glover, made a short speech in Latin and introduced to the vice chancellor the new doctors with seemly observations in Latin, of which the following is a rather crude paraphrase or summary:

First, I present to you Albin Haller. Whatever is done in science in France they discuss in his Académie des Sciences; in that society are gathered all those who pursue such studies; over this assembly each year some renowned man presides. As he is worthy of such a distinction we to-day honor him and ourselves. Wilder Dwight Bancroft follows, our colleague in study and of our own kin, who, a second Ulysses, skilled in many things, adorns a new Ithaca with modern science. Next comes Ernest Julius Cohen from Holland, whose intellect, like that of Ovid, compels him to tell of the changed forms of new compounds. Another Frenchman follows, a professor in the Collège de France at Paris, Charles Moureu, one who by no means despises the most minute of substances but keenly investigates their ways.

To-day, while far-off Etna thunders with dreadful destruction we greet with special fervor an Italian, Rafael Nasini, whom the Etruscan city, Pisa, well known to Virgil, has sent to us. He has chosen for study the volcanic vapors which are poured from the bowels of the earth towards the heavens and Albunea exhaling its dense gas. Now a Swiss approaches, the senior professor of the University of Geneva, Amatus Pictet, who has searched out the very foundations of matter, investigating the facts of the most rarefied vacuum. Next comes a professor from the Academy of Ghent, whose work there are many here present capable of explaining more fluently than I can; it is agreed by all who are engaged in that branch of knowledge that none excels Frederic Swartz. Blessed is that man who knows the causes of things.

The fates do not give everything to all men; I was born in Arcadia, an unworthy student of the ancient Muses, happy to officiate in my little temple. You, who have done such great deeds, forgive me if, ignorant of the various languages you speak, I bid you all welcome in Latin.—[*Chem. Ind.*, **42**, 645 (1923)]

SCIENTIFIC SOCIETIES

Report of Chemical Control Committee of National Fertilizer Association[1]

As stated in the report of last year, a committee known as the Fertilizer Committee on Definition of Terms and Interpretation of Results, has been appointed by the Association of Official Agricultural Chemists to recommend to the association definitions and rulings relating to fertilizer control and inspection laws of the various states. This action is important to the fertilizer industry in order that debatable questions relating to definitions, etc., can be decided more promptly. This committee has submitted the following definitions:

BASIC PHOSPHATIC SLAG—Basic phosphatic slag is a by-product in the manufacture of steel from phosphorus-containing iron ores. The product should be finely ground, and should contain no admixture of materials other than what results in the original process of manufacture. It should contain not less than 12 per cent of total phosphoric acid, not less than 80 per cent of the total phosphoric acid should be soluble in 2 per cent citric acid solution, according to the Wagner method of analysis. Any other phosphatic slag not conforming to this definition shall be designated as low grade.

INTERPRETATION OF THE WORD "LIME" AS APPLIED TO FERTILIZERS—The term "lime" shall not be used in the registration, labeling, or guaranteeing of fertilizers or fertilizing materials, unless the "lime" is in a form to neutralize soil acidity, such as the oxide, hydroxide, or carbonate, or equivalent magnesia compounds.

DEFINITION OF DRIED PULVERIZED OR SHREDDED MANURES—Dried pulverized or shredded manure shall be only what the name indicates, and not mixtures of pulverized manures and other materials.

Definitions for the following subjects have been proposed but not yet formulated—unleached wood ashes, leached wood ashes, ashes from leached wood, double manure salts, manure salts, dissolved bone and potash.

The following questions have also been considered:

(1) Shall the committee encourage and urge the practice of including the formula grade of fertilizer with the brand name? The committee recommends and urges the practice of including the formula grade of fertilizer with the brand name, depending upon the section of country where the product is sold—for example, 4-8-4 or 8-4-4.

(2) The question of a uniform plan of reporting fertilizer analysis in control work. What should constitute a proper detailed analysis report? The committee would encourage not only a study of the quantity of plant food guaranteed in any fertilizer, but also a study of any methods that might result in the improvement of the quality of said plant food, even though this was not called for in the fertilizer law.

(3) Interpretation of results on nitrogen availability.

The by-laws of the association have been amended to provide that fertilizer definitions or interpretations shall not be adopted as official, or an official definition or interpretation be amended, until such definition or interpretation has been recommended by the Fertilizer Committee on Definitions of Terms and Interpretation of Results at at least two annual meetings.

The following recommendations of the association will be of interest:

NITROGEN—It was decided that the referee for 1923 be instructed to study the Devarda method as applied to commercial nitrate; that the Moore method for nitrogen be studied with the collaborators next year; that the use of sodium thiosulfate as a substitute for sodium or potassium sulfide be studied.

PHOSPHORIC ACID—In the determination of insoluble phosphoric acid in precipitated phosphates, the official method was finally modified to provide that the present official method for determination of insoluble phosphoric acid in fertilizers be employed, with the exception that 1-gram samples instead of 2 grams be used.

It was tentatively decided, subject to final adoption this year, that the neutral ammonium citrate solution may be prepared by the method proposed by the special committee appointed to study this subject, in which phenol red is used as an indicator, and the solution compared to a buffer solution prepared from dihydrogen potassium phosphate. The committee did not recommend at present the abandonment of the present official method for making this solution.

POTASH—It was decided that the centrifugal method proposed by Sherrill be discontinued; also that the referee for the coming year study the literature with regard to the use of alcohol stronger than 80 per cent for washing the potash precipitate, with a view to ascertaining if collaborative investigation of this matter is desirable.

The Chemical Control Committee has decided to make a further study of the methods employed for the determination of iron and aluminium in phosphate rock, with a view of recommending some one method as official. At the present time various methods are employed, results from which are not in good agreement, and there seems to be a need for further work on this subject.

It also recommends that in case of determination of sulfur in pyrites, either one of the two following methods be used:

(1) The method of Allen and Bishop, entitled "An Exact Method for the Determination of Sulfur in Pyrites Ores," as fully detailed in the Proceedings of the Eighth International Congress of Applied Chemistry, Vol. 1, p. 33.

(2) Allen and Bishop method, modified by Moore, THIS JOURNAL, **11**, 45 (1919).

While comparatively little pyrites is being used by the fertilizer industry at this time, it is recommended that in contracting for pyrites it be stipulated in the contract that the sulfur shall be determined by either of the two methods mentioned.

The committee also recommends that whenever cottonseed meal or any vegetable meal or organic material is sold on unit basis for potash as well as ammonia, it be stipulated that only water-soluble potash be determined by the official method of the Association of Official Agricultural Chemists.

C. F. HAGEDORN, *Chairman*
J. E. BRECKENRIDGE
F. B. CARPENTER
W. D. RICHARDSON
E. W. MAGRUDER

Officers of Western New York Section

At the annual meeting of the Western New York Section of the AMERICAN CHEMICAL SOCIETY, the following officers were elected:

Chairman: G. P. FULLER
1st Vice Chairman: J. A. HANDY
2nd Vice Chairman: F. L. KOETHEN
Secretary: R. W. HESS
Treasurer: R. A. NELSON
Executive Committee: M. J. AHERN, H. N. GILBERT, J. R. MACMILLAN
Councilors: C. G. DERICK, WALTER WALLACE, A. M. WILLIAMSON

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[1] Presented at the [illegible]th Annual Convention of the National Fertilizer Association at White Sulfur Springs, W. Va., week of June 11, 1923.

NOTES AND CORRESPONDENCE

Regarding Iridium

The present agitation in the organs of the jewelry trade for the passage of a National Stamping Act, restricting the use of the word "platinum" to the pure metal and its alloy with iridium, taken in connection with the statistics of the platinum metals just released by the U. S. Geological Survey, should attract the attention of all chemists and all who are interested in those electrical and scientific industries which call for the use of platinum-iridium alloys.

These statistics show that in 1922 the amount of "new" iridium obtained by the refiners was only 210 ounces, compared with 465 ounces five years ago. The amount of "secondary" metal recovered (largely from scrap) was 1937 ounces, against 3410 ounces in 1918. Imports were 1129 ounces in 1922 and 1345 in 1921. Comparing the amounts available for the past two years, we have 3407 ounces in 1921 and 3276 ounces in 1922.

On the other hand, the consumption in the jewelry industry was 2367 ounces in 1921 and 2588 ounces in 1922; in the electrical industry in 1921, 1003 ounces, and in 1922, 1537 ounces.

As a source of supply Russia is practically cut off probably for at least several years to come, the amount of iridium in the rather precarious supply of Colombian platinum is not large, and Tasmania, the only dependable producer of iridosmium, furnished only about 2000 ounces of this alloy in 1920. It is easy to see that the consumption of iridium is far exceeding the production.

Obviously, a law legitimizing iridium in jewelry platinum and tabooing the other metals of the group as hardeners for platinum, would result in the appropriation of the whole iridium supply by the jewelers, leaving the electrical and scientific industries, where a decided amount of iridium is indispensable in platinum alloys, absolutely crippled. *Verbum sap.*

Jas. Lewis Howe

Washington and Lee University
Lexington, Va.
June 29, 1923

Calendar of Meetings

American Ceramic Society—Summer Meeting, Toledo, Detroit, and vicinity, August 8 to 11, 1923.

American Institute of Mining and Metallurgical Engineers, Inc.—Ontario and Quebec, Canada, August 20 to 31, 1923.

American Chemical Society—66th Meeting, Milwaukee, Wis., September 10 to 15, 1923.

American Association for the Advancement of Science—77th Meeting, Los Angeles, Calif., September 17 to 20, 1923.

Ninth National Exposition of Chemical Industries—Grand Central Palace, New York City, September 17 to 22, 1923.

American Electrochemical Society—Fall Meeting, Dayton, Ohio, September 27 to 29, 1923.

Importance of Diffusion in Organic Electrochemistry—Correction

In the article under this title [This Journal, **15**, 605 (1923)] Equation 2 should read:

$$l = 66\ DC\ \frac{2 \times 96{,}500}{1000 \times 2^* \times 86{,}400\ I} = 0.0737\ \frac{DC}{I} \quad (2)$$

The calculated results given in the article are correct as printed.

Robert E. Wilson
Merrill A. Youtz

Whiting, Ind.
July 7, 1923

The Magic Wand

Editor of Industrial and Engineering Chemistry:

We are interested to note on page 488 of the May issue of This Journal, a brief article by Harvey A. Neville, of Urbana, Ill., on "The Magic Wand," the construction of which he describes in detail.

For your information we would call your attention to patent to J. J. Porter, No. 1,401,185, applied for December 3, 1919, and granted December 27, 1921, describing a magic wand involving the same principles, and call your attention to the fact that a number of the claims of this patent, which is the property of this company, were intentionally drawn broadly enough to cover just such modifications of the patented inventions as the construction described in the Neville article.

Harold M. Porter

The Porter Chemical Company
Hagerstown, Md., June 7, 1923

Editor of Industrial and Engineering Chemistry:

I have had no intention of manufacturing or selling the article described. It is a simple piece of apparatus that anyone can make for his own use. It was designed here for use in our Chemical Open House or Exhibition, and for lecture demonstration in elementary chemistry. Whether or not the patent claims will cover this type of rod I am not prepared to say.

I was not aware previously that any such article had been patented and I appreciate your calling my attention to this fact.

Harvey A. Neville

University of Illinois
Urbana, Ill., June 14, 1923

Bureau of Physico-Chemical Standards

The Bureau of Physico-Chemical Standards, established by the International Union of Pure and Applied Chemistry, with headquarters at the University of Brussels, has samples of the following standard substances available for distribution to the chemists of those countries belonging to the Union:

(A) Standard substances prepared at Brussels and intended primarily for the calibration of low temperature thermometers.

The freezing points of the following substances reproduce to 0.1° C., the scale of the helium thermometer of the Cryogenic Laboratory of the University of Leyden [*Compt. rend.*, **174**, 365 (1922)]:

	° C.		° C.
Carbon tetrachloride	−22.9	Carbon disulfide	−111.6
Chlorobenzene	−45.2	Ether (stable form)	−116.3
Chloroform	−63.5	Ether (metastable form)	−123.3
Ethyl acetate	−83.6	Methylcyclohexane	−126.3

Fifty cubic centimeter samples of each of these substances are available at 25 Belgian francs per sample. All orders should be addressed directly to the bureau.

(B) Supplementing the preparations of the bureau are the following standard materials prepared by the U. S. Bureau of Standards at Washington and obtainable directly from that bureau [*Bur. Standards, Circ.* **25**]: cane sugar, for calorimetry and saccharimetry; naphthalene, for calorimetry; benzoic acid, for calorimetry; sodium oxalate, for oxidimetry; dextrose, for use as a reducing agent; benzoic acid, for acidimetry; tin, zinc, aluminium, copper, and lead, with stated melting point, for use in thermocouple calibration.

The Bureau of Physico-Chemical Standards plans to act as a center for the study of pure materials, and it requests that authors of papers in this field send reprints of their papers to the bureau. It also hopes that industrial organizations may be willing to contribute to the bureau materials which may be used as the starting point for the preparation of highly purified substances.

WASHINGTON NOTES

C. A. Browne to Head Bureau of Chemistry

Charles Albert Browne, for sixteen years chemist in charge of the New York Sugar Trade Laboratory, resigned from that position on July 10 to become chief of the Bureau of Chemistry. It is expected that Dr. Browne will take up his new duties in the fall. He succeeds C. L. Alsberg, the position of chief having been vacant for two years.

Dr. Browne was fitted from birth for such a position, having been born on his grandfather's farm near North Adams Mass., August 12, 1870, the son of a chemical manufacturer and the grandson of a farmer. His first acquaintance with chemistry came about through the fact that his father, an inventor and manufacturer of explosives, lost his eyesight and the younger Browne was called into service at the age of ten years to read to his father from the then standard Fownes "Chemistry for Students." His early life on a New England farm brought him in close touch with the various chemical processes which in those days were carried out by the farmers themselves, such as cider, vinegar, and soap manufacture, so that it was but natural that his studies at Williams College should be directed along chemical lines. From Williams he received the degree of A.B. in 1892, and that of A.M. in 1896. During the interim he spent two years in a New York laboratory as an analyst and a year as instructor in qualitative analysis at the Pennsylvania State College. Later he was chemist at the Pennsylvania Experiment Station. During 1900–1902 he studied with Tollens, a pupil of Fittig, in the University of Göttingen, receiving the degrees of A.M. and Ph.D. from that university in 1902.

C. A. BROWNE

From this time on his attention was devoted principally to the chemistry of sugar. Successively he occupied the positions of research chemist at the Louisiana Sugar Experiment Station, chief of the Sugar Laboratory of the Bureau of Chemistry, and his present position of chemist in charge of the New York Sugar Trade Laboratory. However, despite his active work in the field of sugar chemistry, he has found time to indulge his hobby of the history of chemistry throughout his busy career. His many publications, both of research and historical data, attest his industry and interest in his chosen field. Not only has he found time for many publications, but he was largely instrumental in forming the Section of History of Chemistry of the AMERICAN CHEMICAL SOCIETY, of which he was chairman until his resignation on May 23, and in 1904 his exhibits of sugar at the St. Louis Exposition won him both the gold and silver medals.

Dr. Browne is now chairman of the New York Section of the AMERICAN CHEMICAL SOCIETY, associate editor of the *Journal of the American Chemical Society*, member of the Advisory Board of *Industrial and Engineering Chemistry*, a member of the Executive Committee of the Sugar Division, and for the past three years has been a councilor from the New York Section. He has always been active in SOCIETY matters, having at one time been chairman of the Committee on International Normal Weight for Saccharimetric Sugar Solutions, a member of the Priestley Memorial Committee, and also of the Committee to Formulate Specifications for the Construction of a Polariscope for Laboratory Use.

The opportunity offered for a wider interest and wider service prompted the change, according to Dr. Browne. It is confidently believed that the wealth of experience which he brings to the bureau will make for its continued growth and usefulness under his direction.

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RUBBER SURVEY

W. L. Schurz, United States Commercial Attaché to Brazil, is in charge of the field expedition that is to investigate the Amazon rubber region in behalf of the Department of Commerce. He will be assisted in this work by O. D. Hargis, rubber plantation expert, and C. F. Marbut, of the Bureau of Soils, Department of Agriculture, who will make a study of the soils of this region in reference to rubber production. This party will coöperate with four experts from the Bureau of Plant Industry—Carl D. La Rue, James R. Weir, E. L. Prizer, and M. K. Jessup—whom the Department of Agriculture has sent to Brazil to make a biological study of rubber plants in the Amazon Valley. They sailed from New York direct for Para about the middle of July and will probably be gone about eight months.

D. M. Figart, a special agent of the Department of Commerce who is well known in Far Eastern circles, sailed from the United States last month on his way to southern India, Ceylon, British Malaya, and the Dutch East Indies, where he will make a comprehensive study of all phases of the rubber industry.

Two other parties, one for northern South America, Central America, and Mexico, and one for the Philippines, are being planned.

Several months ago Harry N. Whitford, professor of tropical forestry, Yale University, was appointed by the Department of Commerce and placed in charge of the investigation of sources of crude rubber and the possibilities of developing rubber plantations in the Philippine Islands and in Latin America. J. J. Blandin, formerly in charge of rubber plantations of the Goodyear Tire & Rubber Company, was designated as his assistant.

ALCOHOL TRADES ADVISORY COMMITTEE MEETS

On July 10 and 11, the Alcohol Trades Advisory Committee, recently appointed by the Commissioner of Internal Revenue, D. H. Blair, met at the Hotel Washington, Washington, D. C., to prepare its progress report upon Regulations No. 60, revised, for the manufacture, use, and distribution of alcohol for industrial purposes. Upon the presentation of the committee's preliminary report, the commissioner expressed himself as well pleased with the progress made.

BIBLIOGRAPHY OF BIBLIOGRAPHIES ON CHEMISTRY

A resumé of the literature of the problem in which he is interested is the first need of every research worker in chemistry and chemical technology. To meet this need it is necessary either to find or compile a bibliography of the subject. Unless the problem is very specialized, or of very recent interest, the chances are that somewhere is a list of references, more or less complete, bearing directly or indirectly upon the topic. To believe that it is *somewhere* is an incentive to the search, but to know *where* it is, is to eliminate the search and arrive at the goal.

About two years ago the Research Information Service of the National Research Council enlisted the help of several men in the preparation of a key to scientific bibliographies, each man undertaking to prepare the work in his respective science. The bibliography of bibliographies on geology is now in press and active work is under way in those for chemistry and chemical technology, astronomy, and physics.

In the field of chemistry and chemical technology about six thousand references have already been collected, including separate bibliographies, lists of references appended to articles or books, and comprehensive reviews of the literature. This field is so wide and the subjects covered so numerous that the coöperation of the specialists in the various branches would be very desirable. If *you*, the *reader*, have references to bibliographies in your special field, you will facilitate the completion of this work by sending such references to the compiler of the Bibliography of Bibliographies in Chemistry and Chemical Technology at the National Research Council, 1701 Massachusetts Ave., Washington, D. C. Any annotation which you may make on the completeness or value of the references will be appreciated.

Specifications for Lubricants and Liquid Fuels

A revision of federal specifications for gasoline, kerosene, fuel, and lubricating oils to become effective January 1, 1924, was recommended by representatives of the petroleum industry of the country at an open meeting of the Committee on Lubricants and Liquid Fuels of the Federal Specifications Board held in the Interior Department Building, Washington, D. C., on July 11. N. A. C. Smith, petroleum chemist of the Bureau of Mines and chairman of the committee, presided over the meeting which was attended by thirty-five representatives of the United States Government, of trade associations, of the petroleum industry, and private individuals.

The concrete recommendations made are that a limit of 0.1 per cent be placed on the total sulfur in all grades of gasoline, this to be determined by the lamp method; that the unsaturation test be eliminated or made more lenient; and that the specification for motor gasoline be known as United States government motor gasoline. The only other change of importance recommended in regard to gasoline was to discontinue the use of cotton on the bulb of the distillation thermometer.

The refiners also recommended that the sulfur limit on kerosene be raised to 0.125 per cent, and that the burning test be increased to 16 hours. It was recommended that the committee follow the recommendation of the signal section of the American Railway Association in regard to the specification for long-time burning oil.

The main change recommended on lubricating oils was that the new method of the American Society for Testing Materials for determining color be employed. A discussion of carbon residue limits in the various oils followed. Little discussion of fuel oils occurred.

The recommendations of the petroleum industry were given consideration at a private meeting of the Committee on Lubricants and Liquid Fuels held on July 12.

Industrial Films

Eighty different industrial motion picture films, valued at nearly $200,000, are now in the possession of the Bureau of Mines. These motion picture films were produced at small cost to the Government, practically the entire cost being borne by the various industries filmed. Each film depicts the various processes employed in the manufacture and marketing of some well-known American product wholly or partly of mineral origin. The films are loaned free to technical societies, commercial organizations, colleges, schools, and churches.

Applications for these films should be addressed to the Department of the Interior, Bureau of Mines, Pittsburgh, Pa.

Constants and Conversion Factors

The editorial office of International Critical Tables has prepared for use by the coöperating experts who will assemble the various classes of data for the tables, a list of definitions and approved values of general constants of nature, units of measurement, and conversion factors. This list will be found useful by chemists, physicists, and engineers as a convenient and handy source of reference for these quantities and their logarithms. Copies of this pamphlet can be secured by sending 25 cents in stamps to International Critical Tables, National Research Council, Washington, D. C.

Department of Agriculture Fights Boll Weevil

Three DeHaviland 4B planes are being used by the Department of Agriculture at Tallulah, La., to poison the weevils from the air by dusting the plants with calcium arsenate. Several plantations have been mapped for the test, the results of which will be awaited with interest by every one connected with the cotton industry. Four applications of the poison will be made during the season, 5 pounds being used to the acre at each application. The chemical is sifted out of a specially designed hopper while the plane is flying at low altitudes, usually from 50 to 200 feet. Although extremely fatal to the weevils, there is said to be no danger to human beings or to farm animals.

The Department of Agriculture has taken another step in its intensive fight against the boll weevil, and has opened a new cotton boll weevil laboratory at Florence, S. C. The new station is a coöperative project between the Bureau of Entomology of the Department of Agriculture and the South Carolina Experiment Station. E. N. Winters has been placed in charge of the laboratory.

Tariff Commission Hearings and Investigation

A public hearing on the application for a reduction in duty on casein has been announced by the Tariff Commission for August 13. This is the first hearing to be called as a result of the chemical investigations being conducted by the commission under the flexible tariff. Two applications were filed for this hearing—one by a committee representing seventy-five coated-paper manufacturers, and the other by the Ply Wood Manufacturers Association. A decrease of 50 per cent is asked in the duty of 2.5 cents per pound.

A public hearing has also been announced for September 10 in response to an application from the American Nitrogen Products Company, of Seattle, Wash., for an increase of 50 per cent in the duty of 3 cents per pound on sodium nitrite.

The Tariff Commission has also ordered an investigation of metallic magnesium. This action is based on a report from the metals section of an investigation into the application of the American Magnesium Corporation, Niagara Falls, N. Y., which seeks an increase in the duty on this product.

New Treasury Ruling on Dyes

According to a recent ruling by Assistant Secretary of the Treasury Moss, coal-tar dyes and similar products imported under bond when the tariff act of 1913 was in effect, but not withdrawn from bond until after the tariff act of 1923 became effective, must be appraised and duties assessed under the present law. The ruling was made because of an inquiry from the Port of Boston that certain coal-tar dyes and other products were entered in 1919 and appraised at the foreign market value under the act of 1913. The Boston Customs authorities asked whether this merchandise, which remained in bond after September 22, 1923, may now be appraised legally on the basis of the American selling price.

Concannon Made Chief of Chemical Division

Charles C. Concannon, who for the past eight months has been acting chief of the Division of Chemistry of the Bureau of Foreign and Domestic Commerce, has been appointed chief of that division. Mr. Concannon has served with the division since shortly after its creation in 1922. He was first appointed as assistant chief and served in that capacity until the chief, Carl R. DeLong, returned to the United States Tariff Commission, when Mr. Concannon was made acting chief.

Mr. Concannon is a native of Boston. His early education was obtained in the common schools of that city, at the Boston Latin School, and at Harvard University, where he graduated in 1911, specializing in chemistry.

Mr. Concannon has had extensive experience in the chemical field, both in the manufacturing and the merchandizing end. After leaving college he sold heavy chemicals in New England for Brewer & Company, wholesale and manufacturing druggists and chemists, Worcester, Mass., working successively as laboratory chemist, salesman, and assistant manager of their potato starch factory in Maine. Later, he became associated with the Takamine Laboratories, serving from 1916 to 1921 in various capacities. In connection with that work he spent two years in Japan and China. It was because of his intimate knowledge of the chemicals and chemical raw materials produced in the Far East that he was chosen as assistant chief of this division.

Clinedinst Studio

Charles C. Concannon

Since his connection with the Chemical Division he has developed a monthly list of dye imports reaching the Port of New York. That work has now been expanded to include all articles in Paragraphs 27 and 28 of the Tariff Act of 1922, and Mr. Concannon has already formulated plans to secure similar information from all other ports of entry. He has other plans well advanced for increasing the scope of the work of the Chemical Division.

In announcing the appointment, Acting Secretary Drake said: "Mr. Concannon has been active in the organization of the Chemical Division, and is largely responsible for the initiation of special statistical studies of chemical industries in foreign countries, the compilation of the new monthly dye import list, and other improvements."

Thomas W. Delahanty, who has been assisting Mr. Concannon for about three months, has been designated as assistant chief of the division.

July 16, 1923

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Valuation of Imported Chemicals

Importers of chemical products in France often have great difficulties with the customs administration with regard to the duty on products taxed ad valorem. Thanks to an agreement between the customs administration, the union of industrial chemistry, the merchants syndicate, representatives and brokers of chemical and fertilizer products, it has been decided that by writing to the headquarters of the Syndicate of Chemical Products, 4 Rue de Rome, Paris, one can obtain a certificate of valuation, an official document by which the syndicate and the union of industrial chemistry certify that the product imported possesses such a value in the domestic market. The customs administration declares that, except in special cases, this certificate attached to the customs declaration will be accepted. The importers should indicate their name, address, designation of the product imported, the tonnage, the origin of the merchandise, the place of paying duty, and the corresponding French tariff number.

Radioactivity in Nitrate Deposits

M. Stoklasa, whose studies on the effect of radioactivity on biology, especially in plant physiology, are well known, has just made a series of experiments on the efficacy, as a fertilizer, of Chile nitrate.

According to M. Stoklasa, who has examined the different deposits, known as *chaco*, *loza*, *costra*, and finally *caliche*, which is the deposit exploited, nitrates are secondarily of volcanic origin. The presence of ammonia salts, especially the chlorides, in the emissions of volcanoes—and M. Stoklasa has verified this in the eruptions of Vesuvius and Etna—has been confirmed, and in all lavas and cooled products, as in the lower deposits of Chile, large quantities of ammonium chloride are found This ammonium chloride, under the influence of various nitrifying bacteria, is transformed into nitric acid, which acid, in proportion to its production, dissolves the alkaline elements of the rock in order to form nitrates. In addition, M. Stoklasa has verified the presence of radioactivity in each of these beds. He has found the radium content per gram to vary between 80×10^{-12} and 99×10^{-12}. The existence of this radioactivity in the nitrates would have a fertilizer interest, for M. Stoklasa has made comparative experiments on crops, using pure nitrate from the original ordinary chemical and nitrate produced by the electric arc. The radioactive Chile nitrates gave better crop efficiency than the other nitrates.

These experiments confirm what M. Stoklasa has maintained for a long time as to the role of radioactivity in the growth of plants. The crop tests which have been made in various regions have often given contradictory results, but we think that in this domain no definite conclusion either for or against radioactivity can yet be made, since it must be remembered that the experiments are too few in number and too short in duration, and they are based on the total increase of the harvest and not on the content of the useful elements of that harvest (sugar, protein matter, glucosides, etc.).

Search for New Insecticides

The destruction of insects in general, and especially those harmful to agriculture, is exciting the interest of investigators. Arsenic and lead products are always dangerous, and a suitable product in the vegetable kingdom is being sought.

M. Chevalier has studied pyrethrum, which has been employed for a long time as a parasiticide. He has been able to isolate from pyrethrum (chrysanthemum, cinérarifolium) the active parasiticidal principle. This active principle is an oleoresin, nontoxic to man, slightly toxic for animals, and extremely toxic for insects. This oleoresin paralyzes the muscles and has an action comparable with that of veratrine. Investigations are being carried out to find the chemical constituents of this oleoresin, and to see if, by synthesis, it is not possible to find its active principle.

One of the masters of entomology, L. O. Howard, director of the Bureau of Entomology at Washington, is now in France.

Research in Sugars

M. Gabriel Bertrand, by hydrolysis from cellulose paper, has just discovered a new sugar, "procellulose," a sugar which would be a triglucoside reducer and whose constitution would permit an understanding of the intermediate products between the simple sugars and the celluloses.

In this domain of the chemistry of sugars, M. Bridel, on the one hand, and M. Goris, on the other, have discovered a new glucoside whose decomposition products are blue in color. This glucoside, which M. Bridel has called "monotropéine," is extracted from monotropa-hypopitis. The isolation of this glucoside, aside from its own particular interest, is interesting in that it gives general directions on the methods to employ in the research and isolation of new glucosides, in order to avoid the hydrolysis in the course of the isolation and to avoid a confusion which is often produced between the glucoside itself and its decomposition products.

Corrosion in Carbonic Acid Containers

The manufacturers of compressed liquid carbonic acid have often complained of the corrosion of the metallic containers. M. Hackspil, professor at the Faculty of Science of Strasbourg, has recently shown that this corrosion is due to the presence of nitric acid in the liquefied carbonic acid. The carbonic acid is produced in this factory by the combustion of coke and absorption of the carbonic acid produced by an alkaline wash. This wash is then decomposed and the carbonic acid generated is compressed to liquefaction. In the combustion of the coke, nitrous products are formed which are absorbed by the alkaline wash in the form of nitrites and nitrates, and, during the decomposition of the alkaline wash, the carbonic acid entrains nitrous vapors which are compressed with this acid and cause the corrosion of the container, corrosion which may at times be considerable and result in the destruction of the container.

Recommendations of Congress of Industrial Fuel

The Congress of Industrial Fuel, which was held in Paris from June 15 to 19, made several recommendations which may be of interest to the chemists. It urged especially that, for industrial usage, the higher calorific power be used in preference to the other—that is, to the quantity of heat expressed in large calories, liberated by the complete combustion, at constant pressure, of a kilogram of combustible solid or liquid or a cubic meter of combustible gases, the elements of the combustion being taken and the products of the combustion being recovered at the temperature of 0° C. and a pressure of 760 mm. of mercury, the water coming from the humidity or from the combustion of a combustible matter being condensed.

The Congress asked, furthermore, that, for industrial uses, the calorific power be reported on the raw combustible—that is, ashes and humidity included. It asked, likewise, that in the thermal calculations, especially in the calculation of heat of combustion, only the specific heats of Malard and Le Chatelier be used.

The Congress expressed the wish that complete tables be published giving, for combustibles of diverse origin, the elementary composition, the amount of volatile matter, and the higher calorific power.

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I had the honor of attending as a French delegate, at the 4th International Congress at Cambridge. I will leave the report of this meeting to the author of the London Letter.

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M. Jean Perrin, professor of the Faculty of Science of the University of Paris, who formerly attended some conferences in the United States and is one of the masters of the modern atomic theory, has just been elected a member of the Academy of Science.

July 6, 1923

LONDON LETTER

By Hugh Griffiths, 15 New Bridge St., London, E. C. 4, England

Photographic Chemistry

Whatever opinion may be held regarding the Key Industries Act in this country, it may be said that research into many of the industries so protected has received stimulation. The activity in research on photographic chemistry is perhaps not altogether due to the Key Industries Act, but is also a result of the development of aeroplane photography during the war.

A most important conference has just been held in London on the physical chemistry of the photographic process. Eminent workers, such as W. D. Bancroft of Cornell, Luther and Goldberg of Dresden, M. Clerc of Paris, and many others, contributed. Most of the discussion will be of greatest interest to the specialist.

The University of Cambridge has conferred the degree of Doctor of Science on Professor Bancroft, in recognition of his researches in physical chemistry.

Among the recent contributions to photographic chemistry, a most outstanding one is the discovery, by W. T. A. Ermen, of the British Dyestuffs Corporation, that the skin-irritating properties associated with Metol are due to the presence of traces of an impurity. This impurity, a salt of symmetrical dimethyl-*p*-phenylenediamine, has been isolated, and found to be intensely irritating. This discovery was made during an investigation of different methods of manufacturing Metol, when it was found that the Metol produced according to the patented process of Lapworth, in which benzylamidophenol is first methylated in benzene solution with dimethyl sulfate, and the addition product hydrolyzed, was nonirritating, whereas the product obtained by the process of Merck[1] by action of methylamine on hydroquinone, was intensely irritating. This troublesome impurity having been discovered, one of the most serious disadvantages of Metol as a photographic developer can now be overcome.

The Hele Shaw Filter

On June 6, Hele Shaw gave a demonstration with a new filter press that he has designed for chemical purposes. The construction of this press is in some ways reminiscent of the Plauson ultra filter, but it appears to be extremely simple and should be very cheap.

This filter consists essentially of a pack of sheets of waterproof paper clamped between parallel ends. These paper sheets are perforated with a large number of holes, thus forming tubular filtering elements. The larger holes through the pack are fed with the turbid liquid from suitably spaced holes in the press-heads, while the smaller holes serve to take away the filtered liquid.

A small filter shown was about 2 feet 6 inches high by 1 foot square, and filtered at the rate of about 150 gallons per hour. While this filter is most interesting, and apparently has capabilities of fine filtration not easily achieved in other filters, on the industrial scale the greatest problem will be the removal of the deposited solids from the press. It was explained that the solid material could be washed out by a reversal of flow within a few seconds, but industrially this process would not always be suitable.

This "stream-line filter" operates by a process of filtration against the edges of the waterproof sheets, and is therefore quite distinct in principle from the filter press. It also differs in this respect from the Plauson filter, as the filtering surface of this apparatus is really a cellular mass built up of rings of perforated metal.

Low-Temperature Carbonization

The subject of low-temperature carbonization is always with us, and reports are issued frequently of new processes for which more or less extravagant claims are made. These differ usually in the mechanical methods employed in the plant, and, although the installations which have been employed for this type of carbonization are varied in character, it is not often that a new principle is exhibited.

Recently, however, an interesting process has been described by J. S. Morgan. It is well known that the high capital cost and difficulty of operation in low-temperature carbonization plants are really based upon a problem in heat transmission, and the new method consists in employing a bath of molten lead into which the coal is introduced. In the trials it has been found that a decomposition could be achieved in 15 seconds, which in an ordinary retort takes 4 hours.

At present this process is in an experimental stage, but if certain obvious difficulties can be overcome the advantages are obviously considerable.

During the discussion of this paper it was mentioned that a similar process had been employed in the distillation of coal tar, and in other directions, and that, even when using this process for distilling tar, it had been found unnecessary to replace the lead in a period of two years, and no losses of lead could be detected.

Fuel Research

Technical literature has been enlivened during the last few months by the discussion of the theories of Professor Bone, expounded by him in his Cantor lectures. In order to explain the effect of nitrogen in retarding the combustion of carbon monoxide, Professor Bone has collected a considerable quantity of experimental evidence which he considers points to "activation" of the nitrogen. A very cheerful and caustic criticism of this theory has appeared anonymously under the name "Calorifier." Professor Bone has replied with a considerable show of spirit, and the controversy is now in full blast. This discussion at present bids fair to rival the historic controversy between Hantsch and Bamberger in brightening scientific literature.

A considerable amount of publicity has been given to cases of poisoning by ordinary town gas. Since the introduction of the therm system of charging for gas on a calorific basis, the percentage of carbon monoxide in gas has been much larger.

A mild sensation was caused recently by the claim of C. B. Tully, who, working in collaboration with J. H. West and A. Jaques, announced that by the new process it was possible to reduce the percentage of carbon monoxide to insignificant proportions. The details of the process are not yet fully published, but, as originally announced, it appeared that the carbon monoxide in the presence of steam was passed over the catalyst of iron oxide at a temperature of about 500° C., thus resulting in hydrogen and carbon dioxide. It was suggested that the carbon dioxide could be washed out of the resulting gas. This process would have some disadvantages from a thermal point of view, but it appears that the complete process will consist in converting the gas, which is rich in hydrogen, together with carbon monoxide and carbon dioxide, into methane. This last step will probably prove to be the greatest problem, but if a satisfactory solution of this second stage has been reached, then the process will be of considerable importance in this country.

It has been known for many years that if oxygen were sufficiently cheap, some very important improvements could be made in the working of water-gas plants. About a year ago the Woodall-Duckham Company decided to make an investigation of the possibilities of producing cheap oxygen, and recently a paper on this investigation was read before the Institute of Chemical Engineers by T. C. Finlayson. The discussion resolved itself into a consideration of the possibilities of producing cheap oxygen, and a large number of processes were reviewed. In order to make the use of oxygen in the water-gas plant a profitable proposition, it is necessary to be able to produce oxygen for something under 8d. per thousand cubic feet, and it was decided that up to the present no known process would satisfy the requirements. A most interesting investigation, however, was described on the separation of oxygen and nitrogen by fractionation from a solution in oil prepared under pressure. This process seemed for a time hopeful, and from the description given it would seem very attractive for use in such cases where a 50 or 60 per cent oxygen can be used, provided the mechanical details of the plant could be correctly designed.

June 16, 1923

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[1] D. R. P. 260,234 (1913).

Obituary

Parker Cairns McIlhiney

P. C McIlhiney

Thirty years ago I was working in my little laboratory in an old varnish factory, when one morning there appeared at the door a young man of remarkable beauty and expressive and mobile countenance, who said he had been sent by Prof. Elwyn Waller to see if I would give him some authenticated samples of varnish for study. Though I was not then an old man I was double his age; but in spite of that, or perhaps because of it, there speedily grew up between us a quiet friendship which lasted until his death. I was able to give him, altogether, about forty samples of laboratory-made varnishes and japans; and he verified his method for volatile portion, before he published it, on every one of them. This was a fair example of the care and accuracy of his chemical work—a worthy reflection of the teaching of that great analyst, Waller.

Parker Cairns McIlhiney was born in Jersey City, N. J., October 9, 1870. His parents were Scotch-Irish, from Belfast, Presbyterians of the most rigid sort. He fitted for college at the Jersey City High School, and received from Columbia the degrees of Ph.B., 1892; A.M., 1893; Ph.D., 1894. From 1893 to 1900 he was assistant in assaying, then in metallurgy, at Columbia, and the ten years he spent in these laboratories, where he was Waller's favorite pupil, made him one of the most resourceful and skilful analysts I have ever known. From this time until his death, which occurred on June 21, he operated a private laboratory, where, it was well known, he specialized in original work which most analysts had refused. But also for twenty-five years he had been connected with Louis C. Tiffany (Tiffany Studios) in artistic glass, jewelry, and enamels, for which Dr. McIlhiney received silver and bronze medals at the Paris Exposition in 1900. He was also an expert in chlorine manufacture and uses, and in analysis of varnishes and shellac. He long promised us a book on precious enamels, but his health had been failing for several years and he never wrote it. His widow and one son (a Columbia graduate) survive him.

Once in a great while there is a man who is admired and liked by everybody. That was McIlhiney.

A. H. Sabin

Personals

C. F. Chandler has been elected to honorary membership in the Society of Chemical Industry. It is particularly pleasing that in the first election of honorary members to this society an American should be among those chosen.

The degree of doctor of science has been conferred by Williams College on **Edward Bartow,** professor of sanitary chemistry at the Iowa State University.

John A. Gunton is leaving Transylvania College, Lexington, Ky., to accept a position as professor of chemistry at the University of Western Ontario, London, Ont.

G. N. Lewis, of the University of California, has been elected an honorary member of the London Chemical Society.

Edgar F. Seifert has resigned his position with the American Aniline Products Co., Lock Haven, Pa., to accept a position with the By-Products Steel Corp., Weirton, W. Va.

Kenneth E. Bell has resigned his position with the Lewis Recovery Corporation to accept one as chemical engineer for the A. C. Lawrence Leather Co., Peabody, Mass.

P. B. Sadtler, who for some time has been stationed at headquarters of the Swenson Evaporator Co., has opened offices at 136 Liberty St., New York, and 1309 Widener Building, Philadelphia, as the eastern offices of the company.

Elmer D. Merrill, director of the Bureau of Science, Manila, will represent this bureau at the second Pan-Pacific Science Congress to be held in Sydney and Melbourne in August.

Ernest Anderson, for the past three years professor of general chemistry in the University of Nebraska, has resigned to become head of the Department of Chemistry in the University of Arizona.

M. J. Harnist, formerly chief chemist for the Meyer Bros. Drug Co., St. Louis, Mo., has accepted a position as products control chief of the Brooklyn, N. Y., plant of E. R. Squibb & Sons.

Carl W. Nesbitt recently resigned his position with the Atmospheric Nitrogen Corp., Syracuse, N. Y., to join the research staff of the Victor Chemical Works, Chicago Heights, Ill.

Casimir Funk has accepted a call to organize a department of nutrition in the State Institute in Warsaw, Poland. Dr. Funk sailed on July 13 from Quebec and is planning to be away two years.

Edward B. Durham has accepted the position of engineer with the U. S. Smelting, Refining and Mining Co., Kennet, Shasta Co., Calif. He was formerly maintenance engineer for the Standard Chemical Co., Canonsburg, Pa., and since March 1, 1923, has been with the Koppers Co., Pittsburgh, Pa.

C. P. Derluth, who for the past two years has been engaged in the development of the new district offices of the Celite Products Company in the East, has returned to St. Louis to assume charge of the St. Louis district of that company.

P. J. Freeman, for the past seven years engineer of tests at the Pittsburgh Testing Laboratory, has opened offices for private practice as a consulting engineer at 311 Ross St., Pittsburgh, Pa.

F. O. Sprague has resigned his position as consulting chemist of the Transylvania Tanning Co., Brevard, N. C., and will operate a chemical laboratory for the tanneries of the Endicott Johnson Corp., Endicott, N. Y.

Victor Yngve, who has been engaged in cryogenic research at Harvard University during the past year, has accepted a position as director of research for the Manhattan Electrical Supply Co., New York City.

E. C. Gangloff, formerly research chemist with the National Aniline & Chemical Co., is now chief chemist with Dextro Products, Inc., Buffalo, N. Y.

Zen Zuh Li, who has been working for the American Writing Paper Co., Holyoke, Mass., will join the staff of the Northern Paper Mills, Green Bay, Wis., early in September.

C. A. Carlton has resigned his position as chief chemist of the Columbia Tire & Rubber Co., Mansfield, Ohio, and has entered the employ of the Dovan Chemical Corp., 30 Church St., New York, N. Y., as research chemist.

John H. Schmidt has resigned his instructorship in organic chemistry at the University of Wisconsin to accept a position as research chemist with the Redmanol Chemical Products Co., Chicago, Ill.

Charles W. Pugsley, Assistant Secretary of Agriculture, has submitted his resignation, effective October 1, to accept the presidency of the South Dakota State College of Agriculture and Mechanical Arts, at Brookings. Mr. Pugsley will have filled the office of assistant secretary two years at the time his resignation takes effect.

Jacob G. Lipman, of Rutgers College, has been elected a member of the Swedish Royal Society of Agriculture.

BOOK REVIEWS

Thermodynamics and the Free Energy of Chemical Substances. By GILBERT NEWTON LEWIS and MERLE RANDALL. xxiii + 653 pp. McGraw-Hill Book Co., New York, 1923. Price, $5.00.

This book constitutes a highly original contribution to the subject of chemical thermodynamics. It brings together the theoretical considerations developed and the experimental results secured during a long series of years by Professor Lewis and his associates, and supplements them with many new viewpoints and methods of treatment. Its publication may well be regarded as one of the leading scientific events of the year.

The authors have attempted the difficult task of preparing a book which at the same time shall serve as a textbook in chemical thermodynamics and shall present a summary of existing knowledge needed by research workers in that field. For those graduate students who desire an intensive detailed knowledge of the subject, and especially for those who are working or planning to work in this line of investigation, the book is invaluable. Students, however, who seek such a knowledge of thermodynamics as can be secured consistently with a correspondingly thorough study of the many other newly developed topics of physical chemistry, will probably find this full treatment too detailed, and at places too difficult—a condition which, to be sure, can be remedied, as suggested by the authors, by the omission of certain chapters.

It is difficult to single out for mention in a brief review special characteristics of a work which is replete with original features. Mention may, however, be made of the following:

The second law treatment is based primarily on entropy considerations, and the authors make an earnest effort to render this concept concretely intelligible. Yet, however much may be said in favor of the more fundamental character of this concept as a basis for thermodynamics, especially when it is to be applied mainly to physical and engineering problems, teachers who have had experience in the presentation of the subject to chemical students who approach the subject for the first time, will probably agree that greater success is attained by the primary employment of the ideas of heat content, maximum work, and free energy, the entropy principles being subsequently introduced after these concepts are well understood.

The thermodynamic treatment of solutions, both dilute and concentrated, is unusually complete, the concept of activity being fully developed and systematically applied to the deviations of strong electrolytes from normal behavior.

Of great value is the concise presentation of the so-called third law of thermodynamics and the clear statement of the limitations to which that principle appears to be subject. It seems especially unfortunate that the authors should have employed the name "third law of thermodynamics" when the main result of their work is to show that this principle is not a general law of thermodynamics, but is rather of the character of a condition or equation of state, expressing as it does the fact that the entropy of any element is independent of the nature of the chemical substances in which it may exist, provided these exist at the absolute zero in the *pure condition* (as single molecular species) and in the *crystalline state*. The principle is obviously more like the law that the energy of a perfect gas at constant temperature is independent of its pressure and volume than like the first and second laws of thermodynamics, which express a general relation between heat and work (or between corresponding thermodynamic functions). It might well be briefly called the "constant entropy principle" (for pure crystalline substances).

One is also much impressed through the authors' presentation with the very inadequate experimental testing which this constant entropy principle has already received. Its confirmation is thus far mostly confined to elementary substances, very simple inorganic compounds, like carbon monoxide, and to binary saline or polar compounds. It has not even been tested on oxysalts, like potassium chlorate or calcium carbonate, where in the solid state the oxygen probably forms an integral part of the anion, nor with even simple organic compounds like urea or formic acid. It is to be hoped that the authors will soon carry out in their laboratory low-temperature measurements with such substances.

Finally may be mentioned the computations of the free energies of chemical substances to which the last ten chapters of the book are devoted. The tabulation and selection of the available data, the revision of older free energy calculations, and the presentation of a great number of new ones form one of the most important parts of the book.

A. A. NOYES

Reports of the Progress of Applied Chemistry. Issued by the SOCIETY OF CHEMICAL INDUSTRY. Vol. VII, 569 pp. Society of Chemical Industry, Central House, 46–47 Finsbury Square, London, E. C. 2, 1922. Price, to members of society 7s. 6d., to nonmembers 12s. 6d., trade 10s.

This volume is similar in its scope and execution to its predecessors. The field of applied chemistry is covered broadly, as shown by the twenty-four headings, some of them covering more than a single subject. Only slight changes of last year's contents are noted—refractory materials are put with ceramics and building materials, and the subject of explosives has been discontinued. This may be accounted for by the after-war slump and the lessened interest and activities in the subject during peace times. Minor references, however, to this subject are found in the chapter on "Acids, Alkalies, Salts, etc."

The two indexes, name and subject, appear to be quite complete and therefore valuable in their assistance to the interested, though often busy, searcher.

The review, for such it really is, of the developments of applied chemistry during the past year is not only complete, but the coverage of the literature is comprehensive and broad, as evidenced by the numerous references to English, American, German, French, Swiss, and other publications. In a composite report comprising the technical and applied fields so thoroughly one of the most valuable features is the reference to patents and the patent literature. This has been done in a careful and complete manner, judging from the numerous citations made, especially in the chapters on "Colouring Matters and Dyes" and again under "Fine Chemicals and Medicinal Substances."

As a book of general information and of suggestive possibilities for the advancement of chemistry and its application to the arts, it is most valuable and interesting, even to a lay reader. For one who wishes to keep up with the many lines of practical research and acquire a familiarity of the progress of chemistry in its manifold applications either in one's own field of specialization or in general, it is a volume which is well worth careful reading by all and careful study by many, and should be available in all chemical libraries.

R. L. EMERSON

Motor Fuels, Their Production and Technology. By EUGENE H. LESLIE. 681 pp. The Chemical Catalog Co., Inc., New York, 1923. Price, $7.00.

One reads textbooks for the same reason that one rides in the subway, a simple matter of necessity and distinctly not for pleasure. It was, therefore, with a genuine thrill that we found interspersed throughout Dr. Leslie's book numerous courageous, clear-cut criticisms together with thoughtful recommendations. The monotony of technical description is broken again and again by the author's expression of approval or disapproval, given in no uncertain terms. He warns us to look out for the future:

> Great Britain now commands three-fourths of the oil reserves of the world. We must insist upon an open door policy on the part of other nations with regard to development of oil resources by our nationals. Our petroleum reserves are only 9 per cent of those of the entire world.

It brings joy to the soul to read such statements as:

> Many apparatus now in use would never have been built had the designers had even so much as a clear qualitative understanding of basic principles.
>
> The extensive use of the fire still is convincing testimony of the tendency of the human mind to follow the line of least resistance—the rut of precedent.
>
> Much work is done, and published under the guise of that pretty fiction, "petroleum chemistry," that is in reality highly empirical. One starts with a mixture of, he knows not what, and ends up with another, but different, mixture of the same sort.

No one can deny the justice of the author's criticism. His fairness is nicely illustrated by his broadminded discussion of a cracking process that has had a meteoric career, and his discussion of "Alcohol and the Law."

His criticism is constructive, not destructive. He has contributed many valuable suggestions, especially in regard to the distillation of petroleum. He and his co-workers have designed a new vaporizer, a new dephlegmator, and a new fractionator, which give evidence of a sound and scientific basis. His laboratory still and fractionating column deserve special mention; though embodying well-known principles, it is the first time they have been used in oil work. The reader will heartily agree with the author in the following opinion:

> Distillation equipment now in general use in the petroleum industry can hardly be said to be better than crude. The engineering often is excellent in the sense that good materials are used and layout carefully considered, but the fundamental physics and thermodynamics are sadly neglected.

Dr. Leslie's treatment of the production and technology of motor fuels has several decided advantages. He has placed a great deal of weight on his theoretical chapters.

His new method for calculating the factors of rectification is satisfying for at least two reasons—he employs a nomenclature that an ordinary individual can carry in his mind, and he uses no calculus. This last point will gain votes among the old timers, who look upon calculus with a belligerent eye. The chapter on "Fluid Flow and Heat Transfer" contains an excellent resumé of the empirical formulas used, while the chapter on "Thermal Reactions of Hydrocarbons" covers, among others, the author's extensive work upon the subject. These three chapters, together with two excellent chapters on equipment, are worth more than the price of the book, not only to the man working with petroleum, but to every chemical engineer.

Of course, the reader will not always agree with Dr. Leslie. The reviewer, for example, could not see the need of copying the opinion, concerning the value of certain motor fuel patents, by an Englishman who is unfamiliar with patent principles; but "one must crack a few eggs to make an omelet."

The fact remains the book is alive and interesting and will live through its various editions to a prosperous old age.

D. B. KEYES

The Chemistry of Leather Manufacture. By JOHN ARTHUR WILSON. American Chemical Society Monograph Series. 343 pp. The Chemical Catalog Co., New York, 1923. Price, $5.00.

This book is one which no up-to-date leather manufacturer can afford to be without, since it not only summarizes in language intelligible to any educated man the latest views on the theories of leather manufacturing chemistry, but bears throughout the mark of being written by one to whom theory and practice are equally familiar. Views opposed to those of the author are represented with fairness and clearness, and abundant reference is given to original sources.

The admirable photomicrographs of sections of skins of various animals, and of various stages of manufacture, with which the book is freely illustrated, are in themselves an important contribution to scientific knowledge, and should interest the comparative histologist as well as the tanner, though the author describes them as the result of an investigation "still in progress, and far from complete," and their value is much enhanced by the full details of the thickness of the sections, the magnifications used, and the hardening agents, the stains, and the color screens which were used in their production. They certainly give information never before published, both with regard to skin structure and the changes which it undergoes in process of manufacture.

The description of the anatomical structure of skin is followed by that of its chemical constituents, and this, again, by the physical chemistry of proteids, and especially that of collagen, the principal skin constituent, and of its derivative, gelatin. The theory of the swelling of these and other proteids, as originally proposed by the present reviewer, and since so admirably extended and developed by Wilson himself and by Loeb, is of course given a considerable place, but as Wilson himself remarks, "no other theory of swelling has as yet passed the stage of qualitative speculation," while the Procter-Wilson theory is capable of exact mathematical application, and its results are not only confirmed by laboratory experiment, but explain numberless difficulties which arise in manufacture. Wilson's explanation of the theory is extremely clear, and the mathematics, though somewhat complicated, are purely elementary, and, even if omitted, leave the general theory quite comprehensible.

Considerable space is devoted to the consideration of hydrogen-ion concentration, which is justified by the great importance it has recently assumed in practical leather manufacture. The chapters on physical chemistry are fully illustrated by curves showing the differences obtained by varying dilutions and acidities of the solutions employed, and by varying the time of their action; and these, beside the conclusions which Wilson has drawn from them, contain a mass of information about the reactions of leather manufacture which can only be fully utilized as our knowledge of the process increases.

Wilson's views on the theory of tanning are largely based on the Procter-Wilson investigations as to acid and alkaline swelling of proteids, which prove beyond doubt that these effects are subject to the laws of classical chemistry, and not due to some mysterious force of "adsorption" with laws of its own. He shows, as had been already done by Procter, that the so-called "adsorption formula," $W = ax^b$, merely owes its validity to its general adaptability to *any* curve which rises rapidly at first and afterwards more slowly, and that many chemical reactions which are undoubtedly due to ordinary chemical affinity can therefore be represented by it within the limits of experimental error. In itself, it offers no explanation of the reaction which it represents, and does not imply any recognized chemical principle.

In conclusion, it is only right to acknowledge the liberality and public spirit of Gallun & Sons, of Milwaukee, in allowing the publication of so much valuable matter due to research in their laboratories. Such action appears to be less rare in America than in Europe, where it is unusual for any but the universities to publish their results freely, and no doubt the more rapid advance of technical science in the United States is largely due to this fact.

HENRY R. PROCTER

Premier Rapport de la Commission Internationale des Elements Chimiques. 14 pp. Secretarial General, 49, Rue des Mathurins, Paris, 1923.

The committee consisted of F. W. Aston, G. P. Baxter, B. Brauner, A. Debierne, A. Leduc, T. W. Richards, F. Soddy, and G. Urbain. This report gives a table of isotopes and also one of radioactive elements with their principal constants. A revised table of atomic weights is promised for subsequent publication, while provisionally the values recommended are those given in the International Table for 1922.

The table of isotopes is introduced by certain definitions which are of considerable interest, especially to the conservative chemist. "A chemical element is defined by its atomic number"—that is, the order of the element in the periodic table. An element may furthermore be described as single or complex, according as its atoms are all of equal mass or not. "A complex element is a mixture of isotopes." A distinction is thus drawn between atomic weight (the value ordinarily used) and *atomic mass*. The latter is always an exact integral value when referred to $O = 16$, with the exception of H (1.008). Thus chlorine (atomic weight = 35.46) is a complex element made up of two isotopes whose atomic masses are 35 and 37. The table of isotopes gives the numbers and masses of the isotopes of the different elements which have been investigated up to the present, with references to the original publications.

The table of radioactive elements and their constants is very complete. The names "radon," "actmon," and "thoron" are introduced for the three emanations which are isotopes of the element of atomic number 86. Among the constants given are λ (the radioactive disintegration constant); $\theta = 1/\lambda$ the average life; T, the period—that is, the time in which the quantity of radio element is diminished to one-half; α_0, the range in centimeters of the alpha rays at 0° C. and 760 mm. of mercury; V, the velocity of the alpha rays and absorption coefficients for beta rays and gamma rays in aluminium and lead.

"The Committee," it is stated, "hopes that the new International Tables will be favorably received by the scientific world, and that the values adopted will be generally approved." There is no doubt that chemists and physicists will appreciate greatly the information given in the tables, representing as it does the conclusions of the foremost experts in this field.

SAUL DUSHMAN

Taschenbuch für die Farben- und Lackindustrie. Published by HANS WOLFF and W. SCHLICK. 177 pp. **Schreib-Kalender, 1923.** 150 pp. Wissenschaftliche Verlagsgesellschaft m.b.H., Stuttgart, 1923.

These two little books have one outstanding advantage—their combined size and lack of dignity would not prevent anyone, however careful, from taking them direct to his work bench. The first is concerned with descriptions of the raw materials used in the paint and varnish trades, and the second contains a characteristically German pocket diary. Advertisements make up a considerable part of the bulk of the diary. Little can be said of the combination beyond the fact that it is convenient in form. The methods of analysis given are pretty well known generally and the few formulas for varnish manufacture might have been taken from the stock book of any modern varnish plant. One of the striking features of the "Taschenbuch" is the inclusion of the various regulations on the subject of employment as promulgated by the various labor bodies affecting this particular field.

El Arte de Los Metales, translated from the Spanish of ALVARO ALONZO BARBA by ROSS E. DOUGLASS and E. P. MATHEWSON. 14$^1/_2$ cm. × 20$^1/_2$ cm. ix + 288 pp., with index, 2 photographs, reproduction of old title page and 12 old cuts of apparatus. John Wiley & Sons, Inc., New York, 1923. Price, $3.50 in cloth.

There is probably no work of greater historical interest to the student of the origins of chemistry in the Western Hemisphere than the old Spanish treatise upon "The Art of the Metals," first published in Spain in 1640 by Alvaro Barba, Curate of St. Bernard's Church in Potosi, Bolivia. This ancient work is much more than a technical treatise. The entire first book, whose thirty-six chapters make up a third of the volume, is devoted to a consideration of the properties of ores and minerals and to a discussion of the alchemistic doctrines regarding the genesis and transmutation of metals. The opinion, perhaps, that the outgrown theories of old writers are of trifling interest to modern metallurgists may have caused the present English rendering of Barba's philosophical digressions to be performed with less sympathy and care.

On page 23, "la Disquisicion Heliana" of the original is translated "the Hellenic Discourse;" on page 81, "la Disquisicion Eliana" is translated "the Discourse of Eliana." Barba does not write "Disquisicion Helenica" and "Disquisicion de Eliana," as required by the English renderings. The work of Douglass and Mathewson contains many instances of this hit-or-miss method of translation. As any student of the subject knows, the two treatises mentioned by Barba are one and the same, the name being spelled either Elias or Helias and the derived adjective Eliana or Heliana. The work referred to by Barba is the "Nova Disquisitio de Helia Artista Theophrasteo," published first by Hapelius at Marburg in 1606, and reprinted in the Theatrum Chemicum as the "Disquisitio Heliana."

On page 56 is an even more glaring bibliographic error, "El Tratado de Galileo de Galileis" of the original being translated, and also indexed, as Galileo's treatise "De Galileis." Galileo de Galileis is simply a variation of the familiar name Galileo Galilei.

In some cases the translators have done such violence to Barba's language that the entire meaning of the original is distorted. For example, in the description of the cementation process for parting gold and silver (p. 111), the translation reads: "From ground brick and salt, especially Rock Salt, there is prepared that which is called *Cimiento* (Cementation Powder), with which Gold and Silver are parted. The Nitric Acid attracts unto itself the Gold and Silver and alone burns them with the violence of fire." The reader at once wonders where the nitric acid comes from. Barba mentions nothing about it. What he actually writes is: "Atraenla a siestas dos cosas y la calcinan solo con la violencia del fuego," or literally interpreted: "These two substances—*i. e.*, the brick and salt—attract it (the feminine "la" indicating "plata" or silver) to themselves and burn it only with the violence of fire." The faulty rendering which the translators give this passage is a discredit not only to their ability to read Spanish, but to their knowledge of historic metallurgy.

The employment of such modern chemical terms as nitric acid, sulfates, chlorides, sulfides, oxides, etc., in translating a work written nearly two centuries before these words were introduced, is apt to mislead the unfamiliar reader. The class of ores, for example, which Barba from their color termed "pacos" and which the translators call oxides, did not contain their silver in the form of oxide, as one might infer. Klaproth showed over a century ago that the silver in the *pacos* ores exists in the form of minute particles of the native metal.

But, notwithstanding the shortcomings of their work, the translators have rendered a distinct service by calling attention to this long-neglected treatise and placing it before the English-reading public in an easily accessible and moderately priced form.

The reader will find here most interesting historical information regarding the technic of the early Spanish-American processes, which for several centuries yielded the greater part of the world's production of precious metals. He will be surprised at the practical wisdom and acuteness of many of Barba's remarks, whether they are upon the extraction of gold and silver from their ores by mercury according to the common method (Book Two), or according to Barba's own method of pan amalgamation (Book Three), or whether they are upon the reduction of numerous ores by smelting (Book Four), or upon the refining and parting of the precious metals (Book Five).

The typography of the new translation is good, and the reproductions of the twelve interesting old Spanish engravings of furnaces, assaying utensils, retorts, and other apparatus are all well executed. It is a volume which should be found in the library of every American chemist and metallurgist.

C. A. Browne

Principles of Chemical Engineering. By W. H. Walker, W. K. Lewis, and W. H. McAdams. 1st edition. 637 pp. McGraw-Hill Book Co., New York, 1923. Price, $5.00.

This is by all means the best book so far produced on chemical engineering. It defines the work of the chemical engineer and will serve a valuable purpose in standardizing the scope of his professional activities. In view of the fact that this is the first edition, it is unusually free from errors and omissions. Future elaboration of the subjects covered by this book, especially with the addition of new matter by the same authors, should make the work of Lewis, Walker, and McAdams the most authoritative standard for chemical engineering practice.

M. C. Whitaker

The plan of the book, as expressed by the authors in their preface, is to treat from a mathematically quantitative point of view unit "operations common to all chemical industries, rather than details of specific processes," which might or might not be applicable to other problems.

In the first of the five general divisions they make of their subject "the principles of stoichiometry are reviewed, special emphasis being laid upon the utility of the pound mol as a unit for calculation, and the relative ease with which the units of one system may be transformed into those of another system." This division, as well as the others, contains many problems, in which they "believe the reader may find helpful suggestions relative to the plan of an experimental run, the data to choose, and the method of solution and interpretation to adopt. These problems should be looked upon * * * as an integral part of the text vitally illustrative of the subject matter considered."

The second division deals at length with heat transfer and fluid flow and the laws governing them, "because of their fundamental importance."

The third division treats of fuels and their efficient combustion at length.

"Processes of crushing and grinding mechanical methods of separating materials, together with filtration in its many different forms, are given a descriptive treatment" in the fourth division, "with a mathematical analysis when such seemed advantageous."

"Those processes depending upon vaporization," which are the subjects of the fifth division, "are treated from the common standpoint of vapor pressure equilibria." Here are discussed drying, humidification, dehumidification, water cooling, evaporation, and distillation.

While these divisions are in no way marked in either the text or the table of contents, they form the actual framework upon which the subject matter has been placed. Throughout the book, points are brought out by the use of data obtained from the operation of actual commercial tools (which have been freely used as illustrations), and not of theoretical types which would never be met by the practicing engineer.

Handbuch der Saccharin-Fabrikation. (Benzoesäure sulfinid.) By Oskar Beyer. 143 pp. Rascher & Cie., Verlag Zürich and Leipzig, 1923.

According to the author's preface, this little volume is intended to be a supplement to his previous publication on the same subject, entitled "Über die Kontrolle and Herstellung von Saccharin, 1918." If the two parts were combined, with arrangement of the material in a systematic manner, and by improving and extending some of the chapters and shortening others, as the case may be, the whole would be converted in a presentable monograph on saccharin. This review refers to the second part only, which deals mainly with manufacturing processes and analytical methods, brings the bibliography of the first part up to date, and devotes a few short chapters to various developments in the field of saccharin chemistry.

The operations for the manufacture of saccharin and its intermediates are well described and represent actual manufacturing experience. The text is amplified by illustrations of machinery and manufacturing units, as well as by diagrams and lay-outs of complete installations. The yields given for *o*-toluene sulfamide indicate that the methods described do not represent very best plant practice. Inaccuracies have been noted and some of these are briefly referred to in the following lines.

The mechanism of the permanganate oxidation is incorrectly formulated and interpreted. A solution of the alkali salt of *o*-sulfamidobenzoic acid cannot be converted to saccharin by means of hydrochloric acid. Saccharin is formed already in the alkaline oxidation liquor and is present in form of its alkali salt. The statement that the oxidation in acid medium by means of sulfuric acid and bichromate gives poorer results in regard to yield and quality also requires correction. Since 1919 a large percentage of the world's saccharin production is made by this process and the product is of excellent quality.

In the chapter on medicinal derivatives the German product "Chloramin Heyden" is described, but no mention is made that this disinfectant was first introduced into medicine by Dakin under the name of chloramine T.

In general, this brochure should serve a useful purpose to those connected with the use or the manufacture of saccharin. As a detailed description of the manufacture of a synthetic organic chemical with its many ramifications, this volume also commands some general interest.

Jules Bebie

Yearbook of the American Pharmaceutical Association, 1921. Containing the Sixty-fourth Annual Report of the Progress of Pharmacy, and the Constitution, By-laws, and Roll of Members. Corresponding to Volume 69 of the Former Proceedings of the American Pharmaceutical Association. Vol. 10. 710 pp. American Pharmaceutical Association, Chicago, Ill., 1923.

The book contains valuable association data, such as lists of officers and committees of the association, a list of the officers of the association since its organization, an alphabetical and geographical roll of members, both honorary and active, a list of members deceased since the publication of the 1920 yearbook, the constitution, by-laws, and general rules of the association, and the treasurer's report. The major portion of the book—559 pages—is given over to a report on the progress of pharmacy in 1921. One chapter deals with pharmacy in general, and is subdivided into general subjects: apparatus and manipulations; preparations; and new remedies and trade-named preparations. The remainder of the book is devoted to materia medica, inorganic chemistry, and organic chemistry, and contains brief synopses of the literature bearing thereon. A comprehensive subject and author index completes the volume.

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

June

Increasing consumption of **phosphates** for fertilizing purposes in Italy and plans for developing new sources of supply are described. (Pp. 618–9)

The Mysore Distillation and Iron Works, the scheme for which was sanctioned by the Mysore government, commenced operations on January 18. The works have been under construction for three years, and consist of twelve retorts capable of carbonizing 240 tons of wood per day, a distillation plant for the recovery and manufacture of by-products, and a charcoal blast furnace, with a daily output of 60 tons of charcoal pig iron, low in phosphorus and sulfur. Two qualities of **wood tar** will be recovered from the retorting—a "soluble" tar, which will make a good disinfectant, and the "settled" tar, which possesses wood-preserving qualities. The Mysore government is considering a large scheme for the antiseptic treatment of railway sleepers with this wood preservative. (P. 620)

The Messina mine in southern Africa, which ceased operations about the end of 1921, has resumed work and is now able to turn out about 300 tons of **copper** a month. (P. 633)

A feature of mineral production in Rhodesia during the later months of 1922 was the expansion of the **chrome-ore** industry. Since May, 1922, there has been a revival in the demand for chrome ore greater than ever before. (P. 634)

Production of **crude petroleum** in Rumania during the first quarter of 1923 totaled 383,421 metric tons, an increase of 64,394 tons, or about 20 per cent, over the output for the corresponding period of 1921. (P. 635)

During March the Spanish government granted fourteen concessions for **petroleum** drilling. (P. 636)

Three American **oil** corporations are now exploring for oil in the Republic of Panama. (P. 636)

The increasing use of **oil** as **fuel** for steamship propulsion has resulted in the substitution of oil for coal in cooking ranges and appliances in the galleys in Sheffield. (Pp. 636–7)

In order to secure general efficiency in the administration of the fiscal **petroleum** workings at Comodoro Rivadavia, the executive of Argentine has placed the direction of these activities in the hands of a board of directors. (P. 637)

Disinfectants and **insecticides** imported into Angola have been exempted from the payment of import duty. (P. 654)

Among the commodities on which Germany has reduced her export tax are **ferrochromium alloys** made from imported materials, **unmanufactured lead,** and **zinc** from imported raw materials. (P. 655)

The new parliamentary budget of South Africa doubles the import duty on **calcium carbide.** A change is also made in the duties on **paints and colors.** The duty on **motor spirit** is increased 50 per cent, but this increase is not effective until September 1, 1923, whereas the other changes are at present in force. (P. 657)

The **mineral production** of New South Wales for 1922 is valued officially at 14,274,770 pounds—an increase of 266,122 pounds over that of 1921. (P. 669)

Mexican production of **petroleum** during April averaged 100,000 barrels per day. The wells now coming in are, as a rule, of much smaller production than formerly. (P. 705)

There is a good market for American **paints** and **varnishes** in Yucatan. (Pp. 707–8)

The 1923 crop of **pyrethrum flowers** in Japan will amount to 2260 tons, of which about 700 to 800 tons will be required for domestic consumption. (P. 708)

During the last few years the consumption of **nitrogen** in Germany is reported to have doubled. Present plans are to devote a large portion of the great chemical plant known as the Leuna Works to the manufacture of **synthetic urea** by the Haber and Bosh processes. (P. 708)

The Canadian budget proposals for changes in import duties on **colors** and **crude petroleum,** provisionally effective at once, are cited. (Pp. 714–5)

A review is given of the **chemical industry** in the United States, which shows phenomenal development. Exports have registered a steady monthly increase throughout practically the entire field. The increasing demand has been met by fostering a healthy policy in the expansion of production. (P. 740)

That the Chilean **nitrate industry** has almost completely recovered from the disastrous speculative slump of 1921, is evidenced by the fact that the sales effected during the first three-quarters of the present nitrate year, which began on July 1, 1922, are only 15 per cent less than the quantity sold in the same nine-month period during prosperous war years, and represent nearly triple the quantity disposed of during the first three-quarters of the past nitrate year. (P. 741)

The **petroleum** production and trade of the Far East is reviewed. (P. 753)

The process of extracting **oil** by means of shafts or pits sunk to the oil sands is now being used in a field at Wietze, near Hanover, Germany. The oil is obtained by means of a washing system applied after the sand has been brought to the surface. (P. 755)

The production and sale of **mercury** from the Almaden Mines, Spain, continue to show an increase over 1922, and sales are greatly in excess of production. (P. 826)

Official production figures place the output of Mexican **crude petroleum** in March at 12,371,203 barrels, as compared with 11,134,394 barrels in February. (P. 835)

A great increase in the number of applications for drilling permits is reported by the Secretary of Industry and Commerce of the Mexican government. Many of these applications cover territory in which **petroleum** operations have not previously been conducted. The number of drilling permits granted the first three months of the year totaled 234, of which 67 were granted in January, 81 in February, and 86 in March. (P. 835)

A concession for the installation of plants for the extraction of **gasoline** from natural gas has been granted by the Mexican Department of Industry, Commerce, and Labor to Manuel Gomez. According to the terms of the concession, the concessionaire agrees that a sufficient number of plants will be installed within a period of five years to produce at least 25,000 cubic meters of gasoline per year. It is hoped that such concessions will result in a reduction in the domestic price of gasoline. (P. 835)

A recent act of the Philippine legislature requires the registration of all brands of **commercial fertilizers** and the filing of a statement of contents and the source of the imports. (P. 844)

Statistics are given showing the plants in operation and production of Chilean **nitrate** during the current nitrate year to and including April compared with figures for similar periods in 1922. (P. 847)

STATISTICS OF EXPORTS TO THE UNITED STATES

- Canada—(P. 617 and 833)
  - Wood pulp
- Medan, Sumatra—(P. 639)
  - Rubber
- Brazil and Peru—(P. 639)
  - Rubber
- Singapore—(P. 701)
  - Tin
- Brazil—(P. 701)
  - Manganese
- India—(P. 741)
  - Lac
- Finland—(P. 763)
  - Chemical wood pulp
- Chile—(P. 826)
  - Copper ores

SPECIAL SUPPLEMENTS ISSUED

Denmark
Egypt
Germany
The Netherlands
U. S. Trade with Latin America in 1922

Dutch East Indies—Petroleum Production and Trade. *Trade Information Bulletin* **111.**

CURRENT PUBLICATIONS

NEW BOOKS

Absorption of Nitrous Gases. H. W. Webb. 372 pp. Price, 25s. E. Arnold & Co., London.

Alcohol Fermentation. Arthur Harden. 194 pp. Price, 6s. 6d. Longmans, Green & Co., London.

Causes and Prevention of Corrosion. Alan A. Pollitt. 230 pp. Price, 25s. net. Benn Bros., Ltd., London.

Comparisons of Some Methods of Running Water-Gas Plant. James G. King and J. Fraser Shaw. Fuel Research Board Technical Paper No. 6. 31 pp. Price, 2s. 2d. H. M. Stationery Office, London.

Constitution of Matter. Max Born. 80 pp. Price, 6s. Methuen & Co., Ltd., London.

Destructive Distillation of Wood. H. M. Bunbury. 320 pp. Price, $8.50. D. Van Nostrand Co., New York.

Die Entwicklung der chemischen Technik bis zu den Anfangen der Grossindustrie. Ein Technologisch-Historischer Versuch. Gustav Fester. 225 pp. Price, 7s. 6d. Julius Springer, Berlin.

Fortschritte der Teerfarbenfabrikation. Vol. XIII. January 1, 1916, to July 1, 1921. Friedlander. Price, $36.00. Lemcke & Büchner, New York.

Industrial Filtration. Arthur Wright. Modern Library of Chemical, Engineering. Price, $5.00. Chemical Catalog Co., Inc., New York.

Chemische Technologie des Steinkohlenteers. R. Weissgerber. 141 pp. Price, $1.50. Otto Spamer, Leipzig.

Chemistry: Inorganic and Organic, with Experiments. Charles Loudon Bloxam. 832 pp. Price, 36s. J. & A. Churchill, London.

Gesammelte Abhandlungen. I—Untersuchungen über Hydrochinone und Chinone. II—Untersuchungen über Azine und Azoniumverbindungen. F. Kehrmann. 599 pp. Price, 16s. Georg Thieme, Leipzig.

Manufacture of Acids and Alkalies. G. Lunge. Completely revised and rewritten under the editorship of A. C. Cumming. **Vol. I. Raw Materials for the Manufacture of Sulfuric Acid and Sulfur Dioxide.** W. Wyld. 558 pp. Price, 36s. **Vol. V. The Manufacture of Hydrochloric Acid and Saltcake.** A. C. Cumming. 423 pp. Price, 31s. 6d. Gurney & Jackson, London.

Mischen, Rühren, Kneten und die dazu Verwendeten Maschinen. Hermann Fischer. 93 pp. Illustrated. Otto Spamer, Leipzig.

Modern Gas Producers. N. E. Rambush. 545 pp. Price, 55s. Ernest Benn, Ltd., London.

Practical Bacteriology for Chemical Students. David Ellis. 136 pp. Price, 4s. 6d. Longmans, Green & Co., London.

Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics. W. Nernst. Revised by L. W. Codd. 922 pp. Price, 28s. Macmillan & Co., London.

Trattato di Chimica Fisica. Harry C. Jones. Translated into Italian by Michele Giua. 730 pp. Ulrico Hoepli, Milano.

Wärmewirtschaftsfragen. L. Litinsky. 194 pp. Price, $1.10. Otto Spamer, Leipzig.

RECENT JOURNAL ARTICLES

Air Slaking of Lime. F. H. Rhodes, W. H. Jones, and W. R. Dougan. *Chemical and Metallurgical Engineering*, Vol. 28 (1923), No. 24, pp. 1066–68.

Behavior of the Principal Celluloses towards Iodine and Dyestuffs. J. Huebner and J. N. Sinha. *Journal of the Society of Chemical Industry*, Vol. 42 (1923), No. 24, pp. 255T–60T.

Chrome Tanning. XVI. Donald Burton. *Journal of the American Leather Chemists Association*, Vol. 18 (1923), No. 7, pp. 358–71. **XVII.** D. Burton, R. P. Wood, and A. Glover. *Journal of the American Leather Chemists Association*, Vol. 18 (1923), No. 7, pp. 372–89.

Coke Quality and Blast Furnace Operations. F. W. Sperr, Jr., and D. L. Jacobson. *Blast Furnace and Steel Plant*, Vol. 11 (1923), No. 6, pp. 314–18.

Cold, Clean Artificial Gas and a Discussion upon the General Properties of Gaseous Fuels. Alfred E. Blake. *Journal of the American Ceramic Society*, Vol. 6 (1923), No. 7, pp. 808–30.

Color in Relation to Dyeing. Article VIII. J. Merritt Mathews. *Color Trade Journal*, Vol. 13 (1923), No. 1, pp. 1–4.

Combustibility of Blast Furnace Coke. Ralph A. Sherman and S. P. Kinney. *Iron Age*, Vol. 111 (1923), No. 26, pp. 1839–44.

Common Acid Yellows and Oranges. A Brief Consideration of Their Properties and Uses. Part I. George H. Johnson. *American Dyestuff Reporter*, Vol. 12 (1923), No. 14, pp. 487–91.

Coöperation between the Makers and Users of Scientific Apparatus in America. F. K. Richtmyer. *Science*, Vol. 57 (1923), No. 1484, pp. 649–53.

Denatured Alcohol in Canada. Ross E. Gilmore. *Canadian Chemistry and Metallurgy*, Vol. 7 (1923), No. 6, pp. 155–58.

Effect of Time and Temperature upon the Chlorination of Flint Fire Clay. Herbert F. Kriege. *Journal of the American Ceramic Society*, Vol. 6 (1923), No. 7, pp. 850–3.

Equilibrium Diagram of the System Cu_2S-FeS. An Investigation of Reactions Which Have Important Application in the Smelting of Copper Sulfide Ores. Clark B. Carpenter and Carle R. Hayward. *Engineering and Mining Journal-Press*, Vol. 115 (1923), No. 24, pp. 1055–61.

Estimation of Erythrosin. Walter C. Holmes. *Color Trade Journal*, Vol. 13 (1923), No. 1, pp. 4–5.

Extinction of Coal Mine Fires by Means of Liquefied Carbon Dioxide. Charles L. Jones. *Coal Industry*, Vol. 6 (1923), No. 6, pp. 272–79.

Gas Producer Practice Discussed and a Standard Method for Making Heat Balances Suggested. William B. Chapman. *The Glass Industry*, Vol. 4 (1923), No. 7, pp. 123–26.

Historical Review of the Steaming Process in Calico Printing. J. R. Hannay. *Journal of the Society of Dyers and Colourists*, Vol. 38 (1923), No. 6, pp. 169–74.

I Metodi Rapidi di Determinazione del Carbonio negli Acciai e nelle Ghise. I. Musatti and M. Croce. *Giornale di Chimica Industriale ed Applicata*, Vol. 5 (1923), No. 5, pp. 225–33.

La Determination du Pouvoir, Comburivore et le Dosage de l'Azote du Gas d'Eclairage. Maurice Nicloux. *Chimie et Industrie*, Vol. 9 (1923), No. 5, pp. 866–71.

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Use of Rubber Products as Dielectrics. W. S. Flight. *India-Rubber Journal*, Vol. 65 (1923), No. 24, pp. 13–20.

Vulcanization of Rubber. Henry P. Stevens. *India-Rubber Journal*, Vol. 65 (1923), No. 22, pp. 13–19.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Citrus Culture in Florida. H. J. Wheeler. 149 pp. The American Agricultural Chemical Co., Jacksonville, Fla.

Crushers: A 16-page pamphlet descriptive of the Pennsylvania crushers with special reference to their ability to dispose of tramp iron automatically. Published by the Pennsylvania Crusher Co., Philadelphia.

Haubold Self-Unloading Centrifuge. A 9-page catalog published by Emil E. Lungwitz, 90 West St., New York.

Silica Gel: Refining and Recovery of Petroleum Products with Silica Gel. A 35-page bulletin embodying the paper by E. B. Miller presented and discussed at the fifteenth semi-annual meeting of the American Institute of Chemical Engineers. Published by the Silica Gel Corporation, 1100 Garrett Bldg., Baltimore, Md. *Bulletin* 4, July, 1923.

Spray Heads: An 8-page bulletin descriptive of various types of spray heads for producing mists as in sulfuric acid chambers. Published by the Monarch Manufacturing Works, Salmon & Westmoreland Sts., Philadelphia.

Water Treatment: A comparison of the results obtained by the various types of water treatments and the uses to which each is best put. Published by the Graver Corporation, East Chicago, Ind.

1923 "Year Book" Commercial Fertilizer. 162 pp. For free distribution. Walter W. Brown, 4th Floor Hurt Building, Atlanta, Ga.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Atmospheric Conditions and Physiological Effects Produced on Trainmen by Locomotive Smoke in the Aspen and the Wahsatch Tunnels of the Union Pacific Railroad. S. P. Kinney. *Reports of Investigations* **2494.** 13 pp. Issued June, 1923.

Barite and Ocher in the Cartersville, Georgia, District. W. M. Weigel. *Reports of Investigations* **2477.** 11 pp. Issued May, 1923.

Coal-Mine Fatalities in April, 1923. W. W. Adams. *Reports of Investigations* **2483.** 3 pp. Issued May, 1923.

Coal-Mine Fatalities in May, 1923. W. W. Adams. *Reports of Investigations* **2495.** 3 pp. Issued June, 1923.

Coal-Mine Fatalities in the United States, 1922. W. W. Adams. *Technical Paper* **339.** 97 pp. Paper, 10 cents.

Comparison of Gas Masks, Hose Masks, and Oxygen Breathing Apparatus. S. H. Katz and J. J. Bourquin. *Reports of Investigations* 2489. 5 pp. Issued June, 1923.

Dangers of and Treatment for Carbon Monoxide Poisoning. R. R. Sayers and W. P. Yant. *Reports of Investigations* **2476.** 11 pp. Issued May, 1923.

Explosion-Proof Coal-Cutting Equipments Approved Prior to January 1, 1923. E. J. Gleim. *Reports of Investigations* **2481.** (Supplementary to Bulletin 78.) 14 pp. Issued May, 1923.

Explosives Used in April, 1923. W. W. Adams. *Reports of Investigations* **2490.** 6 pp. Issued June, 1923.

Explosives Used in March, 1923. W. W. Adams. *Reports of Investigations* **2478.** 6 pp. Issued May, 1923.

Fluorspar Mining in the Western States. R. B. Ladoo. *Reports of Investigations* **2480.** 35 pp. Issued May, 1923.

Gasoline Saved on Government Trucks by Adjusting Carburetors by Exhaust Gas Analysis. G. W. Jones and A. C. Fieldner. *Reports of Investigations* **2487.** 13 pp. Issued June, 1923.

Globe-Miami Mine Rescue Maneuvers. E. D. Gardner. *Reports of Investigations* **2473.** 4 pp. Issued May, 1923.

Hydrogen Sulfide as an Industrial Poison. R. R. Seyers, C. W. Mitchell, and W. P. Yant. *Reports of Investigations* **2491.** 6 pp. Issued June, 1923.

Motor Gasoline Surveys of 1920 and 1921. N. A. C. Smith. *Technical Paper* **328.** (Sequel to Bulletin 191. Includes list of Bureau of Mines publications on gasoline.) 41 pp. Paper, 5 cents.

Production of Explosives in the United States during the Calendar Year 1922 with Notes on Mine Accidents Due to Explosives. W. W. Adams. *Technical Paper* **340.** 25 pp. Paper, 5 cents.

Quarrying to Obtain a Uniform Lime Product. Oliver Bowles. *Reports of Investigations* **2479.** 6 pp. Issued May, 1923.

Results of Assays of the New Albany Oil Shale. J. R. Reeves. *Reports of Investigations* **2492.** 11 pp. Issued June, 1923.

Survey of Pacific Coast Petroleum Products. Part 2. Lubricating Oils. E. C. Lane and N. F. LeJeune. *Reports of Investigations* **2482.** 26 pp. Issued May, 1923.

The Metallurgical Treatment of Zinc Retort Residues. B. M. O'Hara. *Reports of Investigations* **2475.** 12 pp. Issued May, 1923.

The Pyrotannic Acid Method for the Quantitative Determination of Carbon Monoxide in Blood and Air. R. R. Sayers, W. P. Yant, and G. W. Jones. *Reports of Investigations* **2486.** 6 pp. Issued June, 1923.

The Reduction of Iron Oxides by Fuel Gases. E. D. Eastman. *Reports of Investigations* **2485.** 14 pp. Issued June, 1923.

Underground Ventilation at Butte. Daniel Harrington. *Bulletin* **204.** 131 pp Paper, 25 cents.

Why Not Scrap "the Davy?" J. W. Paul and A. B. Hooker. *Reports of Investigations* **2484.** 3 pp. Issued June, 1923.

Who May Set Off Blasts in Coal Mines? (State regulations relating thereto.) L. C. Ilsey. *Reports of Investigations* **2488.** 9 pp. Issued June, 1923.

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Brass, Bronze, Copper, and Allied Products. Manufactures, 1921. Prepared under the supervision of E. F. Hartley. 18 pp. Paper, 5 cents.

The Rubber Industry. Manufactures, 1921. Prepared under the supervision of E. F Hartley. Paper, 5 cents.

Department of Agriculture

Adulteration of Insect Powder with Powdered Daisy Flowers (*Chrysanthemum leucanthemum* L.) **with List of Literature Cited.** R. C. Roark and G. L. Keenan. *Department Bulletin* **795.** Prepared in coöperation with Insecticide and Fungicide Board. 10 pp. Paper, 5 cents. Revised May 15, 1923.

Apple By-products as Stock Foods. G. P. Walton and G. L. Bidwell. *Department Bulletin* **1166.** 40 pp.

Chemical, Physical, and Insecticidal Properties of Arsenicals. F. C. Cook and N. E. McIndoo. *Department Bulletin* **1147.** 58 pp. Paper, 10 cents. Issued June 9, 1923.

Dusting for Cotton Boll Weevil. B. R. Coad and T. P. Cassidy. *Department Circular* **274.** 3 pp. Paper, 5 cents. Issued May, 1923.

Home Tanning of Leather and Small Fur Skins. R. W. Frey, I. D. Clarke, and F. P. Veitch. *Farmers' Bulletin* **1334.** 28 pp. Paper, 5 cents.

Production of Sirup from Sweet Potatoes. H. C. Gore, H. C. Reese, and J. O. Reed. *Department Bulletin* **1158.** 34 pp.

Studies on Contact Insecticides with List of Literature Cited. C. H. Richardson and C. R. Smith. *Department Bulletin* **1160.** Prepared in coöperation with the Bureau of Chemistry. 16 pp. Paper, 5 cents. Issued May 29, 1923.

Wearing Qualities of Shoe Leathers. F. P. Veitch, R. W. Frey, and I. D. Clarke. *Department Bulletin* **1168.** 24 pp. Issued July, 1923

Department of Commerce

List of Publications of the Department of Commerce Available for Distribution. 21st ed., May 1, 1923. 95 pp.

Petroleum Map of the Dutch East Indies and British Borneo. Compiled by A. T. Coumbe, Jr., Petroleum Division, Bureau of Foreign and Domestic Commerce.

Portuguese East Africa: Its Resources, Industries, and Trade. S. W. Honaker. *Special Consular Report* **85.** 30 pp. Paper, 5 cents.

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Coke and By-products in 1921. R. S. McBride. Separate from Mineral Resources of the United States, 1921, Part II. 74 pp. Published June 14, 1923.

Geology and Ground-Water Resources of Sacramento Valley, California. Kirk Bryan. *Water-Supply Paper* **495.** Prepared in coöperation with the Department of Engineering of the State of California. 285 pp. Paper, 60 cents.

Gold, Silver, Copper, Lead, and Zinc in the Eastern States in 1922. *Mines Report.* J. P. Dunlop. Separate from Mineral Resources of the United States, 1922, Part I. 8 pp. Published June 12, 1923.

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Surface Waters of Wyoming and Their Utilization. Robert Follansbee. *Water-Supply Paper* **469.** Prepared in coöperation with the State of Wyoming. 331 pp. Paper, 40 cents.

Structure and Oil and Gas Resources of Osage Reservation, Oklahoma. David White and others. *Bulletin* **686;** *House Doc.* **1725,** 65th Congress, 3rd session. 427 pp. Paper, $1.75.

The Commercial Granites of New England. T. N. Dale. *Bulletin* **738.** 488 pp. Paper, 50 cents.

The Industrial Utility of Public Water Supplies in the United States. W. D. Collins. *Water-Supply Paper* **496.** 59 pp. Paper, 10 cents.

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Agricultural Chemistry. List of publications for sale by Superintendent of Documents. *Price List* **40,** 15th ed. 6 pp. Issued May, 1923.

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MARKET REPORT—JULY, 1923

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

The general features of the market for industrial chemicals are much the same as those which prevailed during the preceding month. The usual summer dullness has been apparent on all sides and is an extension of the quiet period which has prevailed during the past few months. Most industries appear to be running at reduced capacity and buying in some lines is at a standstill, or only in sufficient quantities to satisfy immediate requirements. With restricted buying in the market, the trend of prices continues downward, imported chemicals leading the decline in prices. The foreign situation continues to be a disturbing influence in domestic business with offerings from abroad steadily lower in price, while the purchasing power of foreign markets is at a minimum.

In many instances manufacturers are now endeavoring to market surplus stocks and are running their plants at minimum capacity. Buyers are therefore little interested in prices and are unwilling to purchase even at what appear to be very attractive prices. It is proverbial that consumers do not buy in a declining market and, until a buying movement begins again, prices will continue to be subject to shading in many lines. In the list of heavy chemicals imported products are quite plentiful and many importers have been forced to sell at a loss in order to move their goods and realize something, rather than pay high storage charges. Domestic makers have been much slower in reducing prices, owing to the fact that operating costs continue at high levels.

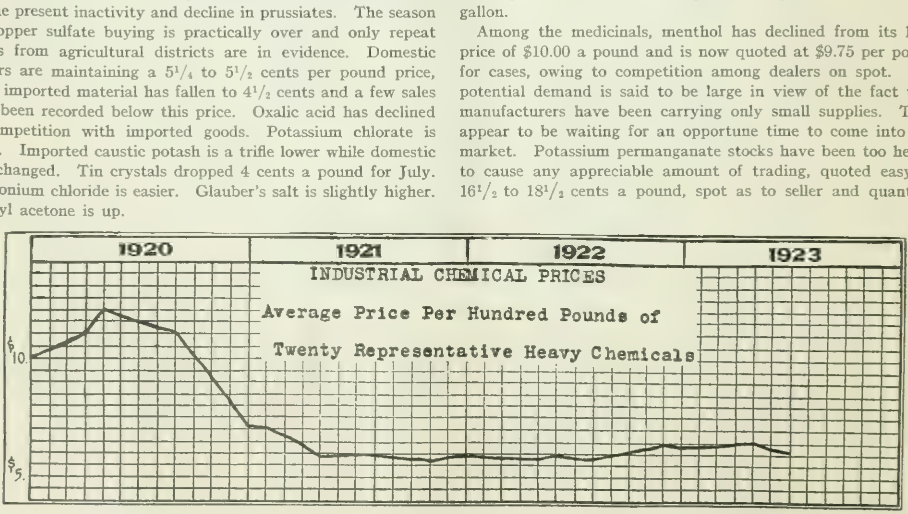
A leading maker of bleaching powder reduced the price of bleach 15 cents, from \$1.90 to \$1.75 per hundred on contract for the third quarter of the year, the action being induced by slowing up in paper and textile mills and a desire to move stocks which are difficult to keep during warm weather. Not all bleach makers followed this reduction and some are still quoting \$1.90. Chlorine was also lower for large lot business. Demand for bichromates has dropped off and makers have reduced prices. Prussiates have been declining steadily. Yellow potassium prussiate has dropped as low as 30 cents a pound and the red is down to 65 cents a pound. Imported sodium prussiate has sold at 13 cents while domestic makers are holding at $15^1/_2$ cents a pound. Lack of demand for prussiate colors is the main reason for the present inactivity and decline in prussiates. The season for copper sulfate buying is practically over and only repeat orders from agricultural districts are in evidence. Domestic makers are maintaining a $5^1/_4$ to $5^1/_2$ cents per pound price, while imported material has fallen to $4^1/_2$ cents and a few sales have been recorded below this price. Oxalic acid has declined in competition with imported goods. Potassium chlorate is lower. Imported caustic potash is a trifle lower while domestic is unchanged. Tin crystals dropped 4 cents a pound for July. Ammonium chloride is easier. Glauber's salt is slightly higher. Methyl acetone is up.

Arsenic prices broke sharply during the month and the market presents a weak appearance. Sales have been made at 10 cents per pound. Supplies have been increasing steadily while demand has been lacking owing to the slowness with which calcium arsenate has been moving this season. Dealers in the South and local markets have been well supplied with stocks of arsenate, but planters have not been buying until absolutely necessary. Evidently, the boll weevil has not been as active this year as was expected. Early estimates predict a larger cotton crop this year than last, which also tends to bear the market in arsenate. Prices are down to 14 to 15 cents per pound in the market.

Crude coal-tar products continue to increase in supply, with consequent reductions in prices. The feature of this market has been the decline in phenol and the entrance of another American manufacturer in the field. The latter openly quoted a price of 35 cents per pound, while another maker is quoting 50 cents per pound. In the open market lack of demand gradually sent the price from 50 cents, which prevailed last month, to 36 cents per pound and less. Another maker of phenol is soon expected to begin operations. Others are reported to be making phenol at present and the situation has eased considerably, though prices are still considered high by many consumers. Cresylic acid has also become more abundant, due to recent importations within the tariff regulations, and prices are on the decline. Sales have been reported at 85 cents per gallon, though most sellers are quoting \$1.00 to \$1.15. Naphthalene has dropped in price with the close of the consuming season for flake material. Dyestuff naphthalene has also been quiet due to inactivity in intermediates and dyestuffs. Benzene and toluene are more plentiful and prices are inclined to be a trifle easier. Xylene is lower.

The market for animal and vegetable oils continued weak and the price trend has been downward. Stearic acid and red oil are easier due to weakness in tallow. Linseed oil is easy due to slow demand at present prices and bearish reports on domestic flaxseed crops. China wood oil is holding up in price due to scarcity, though demand is quiet. Menhaden oil is held at high prices, but buyers say that they will not be interested until lower prices are named. Turpentine dropped to 93 cents per gallon.

Among the medicinals, menthol has declined from its high price of \$10.00 a pound and is now quoted at \$9.75 per pound for cases, owing to competition among dealers on spot. The potential demand is said to be large in view of the fact that manufacturers have been carrying only small supplies. They appear to be waiting for an opportune time to come into the market. Potassium permanganate stocks have been too heavy to cause any appreciable amount of trading, quoted easy at $16^1/_2$ to $18^1/_2$ cents a pound, spot as to seller and quantity.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

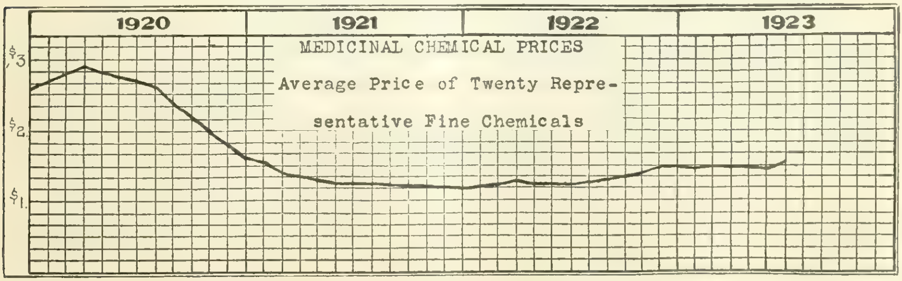
INORGANIC CHEMICALS

	July 1	July 15	Jan. 1923
Acid, Boric, cryst. bbls.......lb.	.11	.11	.11½
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb.	.65	.65	.65
Nitric, 42°, cbys. c/1 wks.lb.	.05¾	.05¾	.06
Phosphoric, 50% tech....lb.	.08	.08	.08
Sulfuric, C. P...........lb.	.09	.09	.07
66° tks. wks.......ton	15.00	15.00	15.00
Oleum, 20%.......ton	19.00	19.00	18.00
Alum, Ammonia, lump.......lb.	.03½	.03½	.03½
Potash, lump...........lb.	*.03¼	*.03¼	*.03½
Chrome...........lb.	.05½	.05½	.05½
Soda, ground...........lb.	.04	.04	.04
Aluminum Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd..lb.	.09	.09	.09½
Chloride, white gran.....lb.	.07½	.07½	.07½
Ammonia, anhydrous........lb.	.30	.30	.30
Ammonia Water, drums, 26°.lb.	.07½	.07½	.07½
Arsenic, white..............lb.	.14	.12	.15½
Barium Choride............ton	*80.00	*80.00	*92.50
Nitrate................lb.	*.07¾	*.07½	*.07½
Barytes, white.............ton	33.50	33.50	33.50
Bleaching Powd., 35%, works ....100 lbs.	1.75	1.75	2.15
Borax, cryst., bbls...........lb.	.05½	.05¼	.05½
Bromine, pure, wks..........lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b. N. Y...................ton	24.50	24.50	24.50
Chlorine, liquid.............lb.	.05¼	.05¼	.05¼
Copper Sulfate......... 100 lbs.	5.60	5.50	6.25
Iodine, resublimed..........lb.	4.55	4.55	4.50
Lead Acetate, white crystals..lb.	.14	.14	.13
Nitrate................lb.	.22	.22	.22
Red.............. 100 lbs.	11.40	11.40	10.60
White (Carb.)..........lb.	.09¾	.09¾	.08½
Lime, live and hydrated, bbl..lb.	.01½	.01½	.01½
Oyster shell............lb.	.03	.03	.03
Lime Acetate.......... 100 lbs.	4.00	4.00	3.50
Magnesium Carbonate, tech..lb.	.08	.08	.08
Magnesite, calcined.........ton	55.00	55.00	55.00
Phosphorus, yellow..........lb.	*.35	*.35	*.28
Red...................lb.	—	—	*.30
Plaster of Paris, tech ....bbl.	3.30	3.30	3.30
Potassium Bichromate.......lb.	.11¼	.11	.10
Bromide, imported......lb.	.18	*.17	.14½
Carbonate, calc., 80–85%.lb.	*.06½	*.06½	*.05½
Chlorate, cryst..........lb.	*.07¼	*.07	*.05½
Hydroxide, 88–92%.....lb.	*.07½	*.07½	*.08
Iodide, bulk, U. S. P.....lb.	3.75	3.75	3.60
Nitrate................lb.	.06½	.06½	.06½
Permanganate, U. S. P...lb.	*.16½	*.16½	*.16
Prussiate, red...........lb.	*.68	*.65	*.90
Yellow.............lb.	*.35	*.32	*.38
Salt Cake, bulk............ton	26.00	26.00	28.00
Silver Nitrate...............oz.	.44½	.44½	.44
Soda Ash, 58%, bags....100 lbs.	*2.00	*2.00	*2.00
Caustic, 76%, N. Y. 100 lbs.	3.70	3.70	3.50
Sodium Acetate.............lb.	.05½	.05½	.07¼
Bicarbonate....... 100 lbs.	2.25	2.25	2.00
Bichromate.............lb.	.08½	.08	.07¾
Bisulfite, powd..........lb.	.04	.04	.04
Chlorate...............lb.	.06½	.06½	.06½
Cyanide, 96–98%.......lb.	.23	.23	.23
Fluoride, tech...........lb.	.09½	.09½	.09½
Hyposulfite, bbls... 100 lbs.	2.90	2.90	3.60
Nitrate, 95%...... 100 lbs.	2.42½	2.42½	2.57½
Nitrite.................lb.	.07½	.07½	.08½
Prussiate, yellow........lb.	.15	.14	.18½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40° ....100 lbs.	.80	.80	.80
Sulfide, 60%, fused......lb.	.05	.05	.05
Strontium Nitrate...........lb.	*.11	*.09½	*.08¾
Sulfur, flowers.........100 lbs.	3.00	3.00	3.00
Crude, mines......long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n....lb.	.11½	.11½	.10¼
Oxide..................lb.	.48	.47	.43
Zinc Chloride, U. S. P........lb.	.25	.25	.20
Oxide, bbls.............lb.	.08½	.08½	.07½

* Resale or Imported (not an American maker's price).

ORGANIC CHEMICALS

	July 1	July 15	Jan. 1923
Acetanilide, U. S. P., bbls....lb.	.35	.32	.35
Acid, Acetic, 28 p. c.... 100 lbs.	3.38	3.38	3.17½
Glacial ....100 lbs.	12.75	12.75	12.05
Benzoic, U. S. P.........lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drums.............lb.	.50	.35	.32
50- to 110-lb. tins...lb.	.57	.57	.34
Citric, crystals, kegs.....lb.	*.52	.51	*.48½
Oxalic, cryst., bbls., wks.lb.	.13	.12¼	.13½
Pyrogallic, resublimed...lb.	1.55	1.55	1.55
Salicylic, U. S. P.........lb.	.40	.40	.45
Tannic, U. S. P., bbls....lb.	.75	.75	.70
Tartaric, cryst., U. S. P...lb.	*.35	*.34¾	*.32
Acetone, drums.............lb.	.25	.25	.21
Alcohol, denatured, complete. gal.	.43	.46	.45
Ethyl, 190 proof, bbls...gal.	4.75	4.78	4.70
Amyl Acetate.............. gal.	3.50	3.50	2.50
Camphor, Jap, refined, cases .lb.	.88	.88	.86
Carbon Bisulfide, c/1........lb.	.06¾	.06¾	.06¾
Tetrachloride...........lb.	.10½	.10½	.10½
Chloroform, U. S. P., drums..lb.	.35	.35	.35
Creosote, U. S. P............lb.	.50	.50	.40
Cresol, U. S. P..............lb.	.25	.25	.25
Dextrin, corn ....100 lbs.	3.79	3.79	3.09
Imported Potato........lb.	.07	.07	.09
Ether, U. S. P., 100 lbs.......lb.	.13	.13	.13
Formaldehyde, bbls..........lb.	.14¾	.14½	.16
Glycerol, dynamite, drums...lb.	.14½	.15	.16½
Methanol, pure, drums......gal.	1.30	1.30	1.35
Methylene Blue, med........lb.	2.25	2.25	2.25
Petrolatum, light amber......lb.	.04½	.04½	.03¾
Pyridine ....gal.	4.00	4.00	2.75
Starch, corn, pow'd.....100 lbs.	3.22	3.22	2.47
Potato, Jap.............lb.	.05	.05	.06¾
Sago....................lb.	.04½	.04½	.03½



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	July 1	July 15	Jan. 1923
Beeswax, pure, white ....lb.	.36	.36	.36
Castor Oil, No. 3............lb.	.14½	.14½	.13
Ceresin, yellow.............lb.	.08½	.08½	.08½
Corn Oil, crude, tanks, mills...lb.	.09⅛	.07¾	.09¾
Cottonseed Oil, crude, f. o. b. mill...................lb.	.10	.10	.09⅝
Linseed Oil, raw, lc/l........gal.	1.12	1.05	.87
Menhaden Oil, crude, mills...gal.	.48	.48	.53
Neat's-foot Oil, 20°.........lb.	.16¾	.16¾	.18½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	5.95	6.00	6.25
Rosin Oil, first run.........gal.	.47	.47	.45
Shellac, T. N...............lb.	.62	.51	.80
Sperm Oil, bleached winter, 38°...................gal.	.99	.99	1.03
Stearic Acid, double pressed...lb.	.13	.13	.12½
Tallow Oil, acidless..........lb.	.10½	.10	.11½
Turpentine, spirits of........gal.	.98	.93	1.56

METALS

	July 1	July 15	Jan. 1923
Aluminium, No. 1, ingots.....lb.	.25	.25	.23
Antimony, ordinary......100 lbs.	6.75	6.75	6.75
Bismuth.....................lb.	2.75	2.75	2.75
Copper, electrolytic..........lb.	.15	.14⅝	.14¾
Lake.................lb.	.15⅛	.14⅞	.14¾
Lead, N. Y.............100 lbs.	7.00	6.00	7.80
Nickel, electrolytic...........lb.	.29	.29	.36
Platinum, refined, soft........oz.	116.00	116.00	118.00
Quicksilver, flask......75 lbs. ea.	67.50	66.00	73.00
Silver, foreign...............oz.	.65½	.63	.63
Tin.........................lb.	.40⅝	.38	.39
Tungsten Wolframite....per unit	8.50	8.35	7.50
Zinc, N. Y.............100 lbs.	6.10	6.50	8.25

FERTILIZER MATERIALS

	July 1	July 15	Jan. 1923
Ammonium Sulfate, expt.100 lbs.	3.50	3.50	3.90
Blood, dried, f. o. b. N. Y...unit	3.75	3.75	4.70
Bone, 3 and 50, ground, raw..ton	28.00	28.00	28.00
Calcium Cyanamide, unit of ammonia..................	2.25	2.25	2.25
Fish Scrap, dried, wks.......unit	4.00	4.00	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.25	3.25	3.00
Florida, 70%...........ton	3.55	3.55	3.55
Florida, 74–75%........ton	4.50	4.50	4.50
Tennessee, 72%.........ton	5.50	5.50	5.25
Potassium Muriate, 80%....unit	.68	.68	.68
Tankage, high-grade, f. o. b. Chicago...............unit	3.50 & .10	3.50 & .10	4.75 & .10

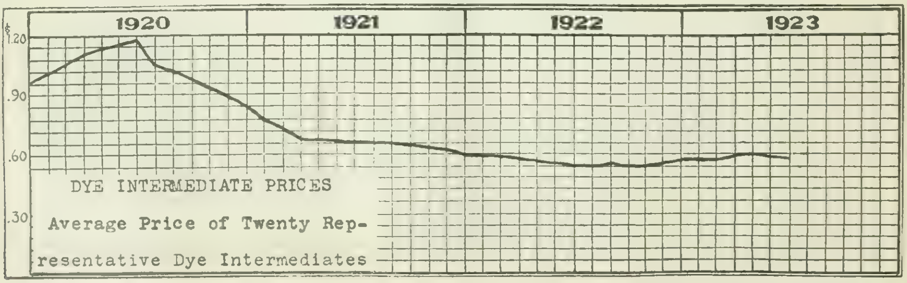
COAL-TAR CHEMICALS

Crudes

	July 1	July 15	Jan. 1923
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.27	.27	.30
Naphthalene, flake...........lb.	.08	.07¼	.06½
Phenol, drums...............lb.	.50	.35	.32
Crudes *(concluded)*			
Toluene, pure, tanks.........gal.	.30	.30	.30
Xylene, 2 deg. dist. range, drums.................gal.	.85	.85	—

Intermediates

	July 1	July 15	Jan. 1923
Acids:			
Anthranilic.............lb.	.96	.96	1.10
Benzoic, tech...........lb.	.70	.70	.65
Cleve's.................lb.	1.00	1.00	1.25
Gamma..................lb.	1.80	1.80	1.85
H......................lb.	.80	.80	.80
Metanilic...............lb.	.60	.60	.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.62	.62	.60
Nevile & Winther's.......lb.	1.25	1.25	1.15
Picric...................lb	.25	.25	.20
Sulfanilic...............lb.	.20	.20	.19
Tobias'.................lb.	1.30	1.30	1.30
Aminoazobenzene...........lb.	1.15	1.15	1.15
Aniline Oil.................lb.	.17	.17	.17
Aniline Salt................lb.	.24	.24	.25
Anthraquinone (sublimed).....lb.	1.30	1.30	1 30
Benzaldehyde, tech..........lb.	.75	.75	.65
U. S. P..................lb.	1.50	1.50	1.40
Benzidine Base..............lb.	.82	.82	.84
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol..............lb.	3.80	3.80	3.75
Dianisidine.................lb.	4.60	4.60	4.50
p-Dichlorobenzene...........lb.	.17	.17	.17
Diethylaniline..............lb.	.60	.60	.60
Dimethylaniline.............lb.	.42	.42	.41
Dinitrobenzene..............lb.	.19½	.19½	.19
Dinitrotoluene..............lb.	.19	.19	.20
Diphenylamine..............lb.	.48	.48	.50
G Salt.....................lb.	.55	.55	.60
Hydroquinol................lb.	1.25	1.25	1.05
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist............lb.	.24	.24	.26
a-Naphthylamine............lb.	.35	.35	.29
b-Naphthylamine............lb.	.75	.75	.95
m-Nitroaniline..............lb.	.78	.78	.80
p-Nitroaniline..............lb.	.74	.74	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol..............lb.	1.00	1.00	.72
o-Nitrotoluene..............lb.	.10	.10	.10
p-Nitrotoluene..............lb.	.60	.60	.65
m-Phenylenediamine.........lb.	.98	.98	1.00
p-Phenylenediamine.........lb.	1.45	1.45	1.50
Phthalic Anhydride..........lb.	.32	.32	.35
R Salt.....................lb.	.55	.55	.55
Resorcinol, tech.............lb.	1.50	1.50	1.50
U. S. P..................lb.	2.00	2.00	2.00
Schaeffer's Salt.............lb.	.60	.60	.60
Sodium Naphthionate........lb.	.62	.62	.62
Thiocarbanilide.............lb.	.35	.28	.35
Tolidine (base).............lb.	.95	.95	.95
Toluidine, mixed............lb.	.31	.31	.30
o-Toluidine................lb.	.15	.15	.15
p-Toluidine................lb.	.90	.90	1.00
m-Toluylenediamine.........lb.	.90	.90	.95
Xylidine...................lb.	.50	.50	.42



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EDITORIALS

Quantity Production

ON every hand we find materials from which we could not benefit but for quantity production, which is symbolic of American manufacture. But quantity production can easily become the stock explanation offered for poor work and thus cease to be a virtue. One may expect certain imperfections in inexpensive articles and have no cause to complain, but what about something costing, say, a couple of thousand dollars? Seldom it is, for example, that an automobile in this class reaches the ultimate consumer in a condition not requiring the attention of a "service" mechanic before a hundred miles have been measured. True, there is a guarantee which permits the owner at his own expense to return the car to the maker, have imperfections made good at a certain charge, and pay return transportation, but these privileges are extended only in case the materials used have been found faulty.

Chemical manufacturers cannot run their plants to overcapacity and depend upon an army of umbrella menders to make adjustments at the buyer's expense after their product has been sold. Unsatisfactory chemical products are returned collect. Quantity production? Why, each pound of a chemical compound contains more molecules than all the cars that will ever be made, and if any considerable number of these differ from the majority, the product is unsatisfactory. There are no service stations for the chemical manufacturer's product, and he works within limits much more narrow than most people realize.

There is one factor in his success which comes to him as the finished product of another—his chemists and chemical engineers. To-day these too are produced in quantity. Is it the best way? One of these days we expect some one to organize a campaign against waste in education. Some taxpayer is going to object to investing three hundred to nine hundred dollars per year per student in addition to what the student himself spends, without some assurance that the investment is sound and that the recipient is one capable of fully utilizing what is thus presented to him. Psychologists can render no more valuable service than by devising methods which will be of assistance in the choice of a career.

Until we find some proper way to designate and select those who are to be fitted for professional careers, quantity production will continue in most educational institutions. Young men and women no longer come into close contact with inspirational professors and leaders. They see the names of department heads on the office doors, but at the time when they most need to catch a real vision they are too often expected to do so by way of a mirror—the part-time instructor. We are getting further and further away from those delightful classes where the professor called us by our first or last names, as might suit his fancy, and knew us as individuals in whom he took a personal interest. To-day classes are more likely to be represented by a card index, reference to which is made when quizzes are held or the results of written examinations recorded.

True, by dealing with a large number of individuals the chances of finding another Faraday are greater. But we still have to solve the problem of quantity production in our educational systems by an inspection which will assure quality with a guarantee that means something.

The New Chemical Exposition

THE National Exposition of Chemical Industries as conceived and conducted as an annual event has accomplished its purpose. The first exposition came at a time when there was a question as to whether America could establish a chemical industry. Were there sources of materials? Could a chemical plant be equipped from the offerings of the apparatus manufacturers? Were the foundries capable of working to chemical plant specifications? And what proof did we have that our engineers could design chemical plants and equipment?

The first exposition greatly helped in answering these and similar questions, and subsequently there were included the products of the infant industry, the growth of which was reflected by the development of the chemical show itself. Thus the annual exposition became a real contributor to the realization of the dream that in the future America must be less dependent upon resources without her borders for materials now known to be indispensable.

Now comes another cycle. After this year the exposition will be on a biennial basis. Service will continue to be the dominant note, but with a much broader emphasis—service to chemical manufacturers, to equipment builders, to buyer and seller, and to those whose products are accessory to the industry. There will be added service to the public and to the student through new educational features, comprising special exhibits, lectures, etc. An interest founded on knowledge on the part of these great groups is vital if our industry is to attain a full measure of success. The extended active participation of the exhibitors in the management of the project is gratifying, and how attentively their suggestions will be heard by those directly responsible for the exposition is shown by this decision to make the affair biennial after this year, this step having been taken following a letter-ballot of the exhibitors.

With conscientious service as its aim, the chemical exposition will succeed in the future as in the past.

Significant Coöperation

CHEMISTRY and Industry for August 3 announces editorially the decision of the Chemical Society to publish in *Chemistry and Industry* abstracts of its papers and discussions. Coöperation between those identified with pure chemistry and those specializing in its application to industry we can heartily recommend to our English friends. The experience of the AMERICAN CHEMICAL SOCIETY is that excellent results are possible through such a unification of interests. The ideal expressed in the editorial that "there should be one organization in every country whose duty it would be to ensure that one abstract and one only should be prepared of all the papers applying to some science," is well-nigh approached in America. Every organization recognizes the authority and excellence of *Chemical Abstracts*, and journals which publish abstracts of chemical articles quite properly use *Chemical Abstracts* as their primary source.

Hereafter, we are to find in *Chemistry and Industry* the news which it now carries, together with information of still more permanent value. We congratulate the societies involved and express the hope that before long there may be still closer coöperation between the chemical societies of Great Britain and the AMERICAN CHEMICAL SOCIETY.

American Potash Production Recognized

LAST year when the fertilizer manufacturers refused to consider American potash when placing their contracts, we had a few things to say on the injustice and unfairness of their course. At this time we wish to be equally clear and emphatic in congratulating those same manufacturers upon their change of policy. We likewise congratulate the producing company for the manner in which it has demonstrated that there can be and is a potash industry in America.

This year in making contracts the fertilizer manufacturers first made due allowance for American production and then arranged for European potash upon what is said to be a joint contract in which both French and German sources of supply are represented. Practically all American fertilizer manufacturers are represented by the associations involved in the transaction. Meanwhile, the quality of our potash is proving most satisfactory, and one consumer that took but 450 tons of K_2O last year has contracted for 1600 tons this year. The early difficulties due to impurities have disappeared.

There is a lesson in all this which we should like to bring home to all manufacturers. We have potash production in America because a group of financiers was willing to invest heavily in chemical research and to back it to a conclusion. They sought good advice, and when they found it they acted upon it. They were willing to let fundamentals be determined in the laboratory and to wait for results. Having secured a man qualified to act as director of research and development, they placed their faith in him and did not interfere with his program. When the results of sound research enabled a plan of action to be determined, they proceeded in a persistent fashion. Sound chemistry and sound finance make a team difficult to defeat. In the present instance the result has been a product which has won its way on quality.

We trust the friendly relations established between producer and consumer may endure and be further strengthened.

Require Demonstration

THE laws of our country obligate the Commissioner of Patents to issue a patent if valid claim is made for something that is new and operable. Dependence is placed upon the literature to disclose to what extent the invention claimed may be a novelty. But whether or not a patent may be operated with the information disclosed is much more difficult to determine in the case of chemical patents than with many other groups. The Commissioner of Patents has the power to demand a demonstration if there is a question as to the adequacy of the disclosure, and in the case of mechanical inventions it is common practice to require a model with which a demonstration can be made. It is obvious that the number of people capable of passing upon the claims of a mechanical invention, for example, is greater than of those who may pass judgment upon chemical inventions.

Experience in a recent suit, in the course of which the judge required a witness to demonstrate in the laboratory whether or not patent disclosures were sufficient to enable the product named to be made, naturally leads to the inquiry: Might it not be better to require a demonstration previous to the issuance of any chemical patent? With the precedent of requiring models for some mechanical inventions but not for all of them, there would seem to be no new procedure involved in making it standard practice for the inventor or his representative to appear before a group of those skilled in the art and show that, upon a small scale at least, the process as disclosed in the claims can be carried out and a satisfactory product obtained. Within the scientific bureaus in Washington are specialists in nearly every branch of chemistry. There are ample laboratory facilities and a considerable amount of equipment on a semiworks-scale, so that no inventor need work at a disadvantage.

Perhaps it is fair to assume that if the applicant resides in America we have within our borders sufficient skill in the art to avoid the difficulties which have already arisen with respect to foreign-owned patents, owing to the well-known fact that in a chemical patent enough information can be disclosed to secure it without divulging the many technical points essential to successful operation. Moreover, it has been demonstrated that so-called patent pirates have no hesitancy in taking out numbers of patents covering a new development in every direction and based on theory or imagination. Such patents become no more than an expensive nuisance to the man who is earnestly perfecting a new product or process.

Anything done to guarantee that if the procedure disclosed in a patent were followed by one reasonably skilled in the art, the results claimed would be accomplished, should be helpful. We suggest a demonstration to prove that it is workable prior to patent issuance. What do you propose?

A Nation Honors a Scientist

THAT a scientist can win the grateful recognition of a nation and be honored as are statesmen, soldiers, and other public servants, is proved by the lengths to which France has gone in acknowledging her debt to Pasteur on the occasion of the one hundredth anniversary of his birth. Reference has been made previously to the various meetings held in his memory, these being attended by high officials, savants, and the public.

It has remained for France to issue a series of postage stamps in honor of a scientist for his contributions to science. We have our series bearing a likeness of Franklin, but it is undoubtedly Franklin, the diplomat, and not Franklin, the man of science, who is thus honored. The Pasteur stamps are attractive in their simplicity, bearing the likeness and the name of the great man. By the issuance of these stamps attention is called to the fact that here is a man who began his career as a chemist, whose services to his country and to the world have been on a par with those of the men customarily singled out for such recognition. We know that his contributions far excel those of the politicians. How true is this statement which is attributed to Pasteur:

> In our century science is the soul of the prosperity of nations and the living source of all progress.
>
> Undoubtedly, the tiring daily discussions of politicians seem to be our guide. Empty appearances! What really lead us forward are a few scientific discoveries and their applications.

Dr. Edgar F. Smith calls to our attention the fact "that this is the centenary of Joseph Leidy, the great biologist, anatomist, and geologist, a man who certainly was regarded abroad as one of the leaders of his age.*** Why could not a similar stamp be brought out by our Government bearing his head?"

In our February number we reproduced a series of cartoons of van't Hoff to emphasize the fact that the appearance of these drawings in the daily press of his time indicated that a scientist could attain prominence in the public eye equal to that usually achieved only by men in public life. There would be no point in this if the publicity and honor for the individual were the goal. But a man cannot be honored without calling the attention of the layman to the science with which he is identified. The science thus becomes a living thing and the good work of other scientists is given support and recognition which means much.

Those who plod on and have not yet been given the recognition which their work merits may be cheered by the old parody which the appearance of the Pasteur stamp recalls to mind:

Lives of great men all remind us
We may yet be shining lamps,
And departing leave behind us
Another face for postage stamps.

Testimony Completed at Wilmington

CONTRADICTIONS between expert witnesses and the resolution of the differences by experimental proof formed a dramatic finish to the taking of testimony in the suit of the United States against the Chemical Foundation, Inc., for the recovery of the seized, enemy-owned patents sold to the Foundation by the Alien Property Custodian in 1919. One of the contentions upon which the Government bases its suit is that the sum paid for these four thousand eight hundred patents ($250,000) was totally inadequate and in no way related to their value. The Government further charges that its agents were not fully informed of the value of the property which they sold. In combatting these contentions the Foundation introduced witnesses to testify that the patents were not complete disclosures of the processes involved, that their value was consequently greatly reduced, and that the government agencies were well acquainted with all the particulars of the transaction.

Evidence presented by the expert witnesses for the defense had tended to show that licensees under the patents had been forced to spend large sums of money to develop workable processes and that these successful procedures often varied essentially from the disclosures in the patents. Following this, the Government offered in rebuttal several witnesses who testified that they had obtained the results shown by the patents by following the exact procedures given therein.

Walter G. Christiansen, of the Harvard Medical School, was one such witness. His testimony was to the effect that he did produce arsphenamine by following exactly the procedure outlined in the patent. According to his testimony, he conducted some twelve hundred experiments with arsphenamine, in six hundred of which he produced this compound following the patent according to his interpretation of it with variations in the technic on which the patent was silent. The results of these experiments have been published from time to time in the recognized journals. It was brought out in the cross examination that there was some question as to whether the "interpretation" did not involve actual essential change in the process, and it was shown by a quotation from the witness's own publications that he had recommended definite additions to the procedure of the patent to get the best results [*J. Am. Chem. Soc.*, **43**, 2202 (1921)]. In general, the evidence of Dr. Christiansen was in contradiction to that of Dr. Stieglitz and others on the same subject.

Principal interest in this part of the trial centered in the request of Judge Morris that Louis Freedman, an employee of the H. A. Metz Laboratories, prepare cincophen under the observation of the court to substantiate his claim, made on the witness stand, that while in the employ of the Calco Chemical Company he had made this product with 60 per cent yield on his first experiment, following the patent exactly. His testimony was contrary to that of M. L. Crossley, chief chemist of the same company, who previously testified that his company had spent some $60,000 perfecting the cincophen process. Upon later examination of Dr. Freedman, when he had the original records of his experiments, it was shown that in the original experiment he had obtained a 50 per cent yield of a crude product which he had noted at the time of the experiment was unsatisfactory both as to quantity and quality.

The experiment by Dr. Freedman was carried out at Swarthmore College in the presence of H. D. Gibbs, expert for the Government, M. L. Crossley and E. K. Bolton, experts for the defense, and Gellert Alleman, of Swarthmore College, expert representing the court. The entire operation was supervised by the United States Marshal. The instructions of the judge were that the experimenter be given everything that he might require, that he produce not more than three batches of cincophen and one batch of pyruvic acid—an intermediate which he testified to have made before starting the actual process of making cincophen—and that the entire group of experts satisfy themselves that all the materials used be of the proper purity, and the experiment on cincophen be carried out strictly in accordance with the patent. This party left the court late on Saturday afternoon for Swarthmore, where the actual experiments continued from early Sunday morning until late Monday morning, July 23.

Dr. Freedman succeeded in preparing two batches of cincophen, both of lower than commercial quality, with yields of 26.9 per cent and 14.3 per cent of theory, respectively. The testimony showed that in the first experiment the only variation from the actual procedure of Example 2 of the patent was that the mixture of aniline and benzaldehyde in alcohol was made by pouring the ingredients together successively rather than simultaneously as the patent states. In the second experiment this deviation from the procedure was rectified, but due allowance was made for the impurities in the pyruvic acid used. All witnesses to the experiments agreed substantially on the results and testified that such a yield as that obtained would not be commercially profitable. Statements were made by some of the witnesses that the quality was not up to the standard, to which Dr. Freedman replied with a grand stand assertion that he stood "ready to consume any amount that any doctor would prescribe." He continued with a statement that he was "put on trial under very severe test at a very unusual time," referring to his approaching marriage. This statement was questioned by the judge, who asserted that he did not consider the conditions of the test especially severe in view of the assertions made by the witness previous to it. Pyruvic acid was produced by the witness, but this was not given prominence in the testimony.

Other witnesses were called during the last two sessions by the Government to show the validity of directions contained in the arsphenamine patents. They included G. W. McCoy, director of the Hygienic Laboratory, W. O. Emery of the Bureau of Chemistry, H. D. Gibbs of the Hygienic Laboratory, and C. N. Myers of the H. A. Metz Laboratories. Interest in their testimony was overshadowed by that in the experiment of Dr. Freedman.

Thus ended the taking of evidence in what is probably the most important legal case ever conducted so far as it relates to the chemical profession. Throughout the trial the court room was the center of interest from the entire chemical industry and profession in America, and there is no doubt that it will continue to be so until final disposition of the case is made. Following the taking of testimony, the case was closed for counsel to prepare briefs for presentation and argument on October 9. It is hardly probable that a decision will be handed down before the end of the year.

Trends in Photochemical Research

By J. H. Mathews

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THE history and progress of photochemistry have been quite similar to the history and progress of other branches of science. First, we have scattered observations, many of them imperfectly made, a gradual accumulation of facts, attempts to work out relationships from these facts, and, finally, the attempt to provide a working theory which will be in accord with the observed facts.

J. H. Mathews

In recent years the interest of photo chemists has turned from the accumulation of facts regarding the synthesis and decomposition (photolysis) of compounds to a study of more fundamental relationships. The number of known photochemical reactions now runs well into the thousands, and many of our ordinary reactions are undoubtedly more dependent on radiation than we realize.

To the mind of the writer there are four fields of photochemistry that transcend all others in present interest and immediate usefulness. Before proceeding to them, however, it should be pointed out that the photo chemist, like the colloid chemist, has gradually enlarged his field so that the present boundaries are far wider than those of a former generation. It is now realized that visible light differs from the ultra-violet, infra-red, heat, and electrical waves only in frequency, and that they are all radiations of the same general character. From the shortest X-rays and rays from radioactive substances to the infra-red, at least, all radiations are capable of producing photochemical changes, and whether a certain reaction will be influenced by radiation is a question of wave length and of the specific reaction involved. While there are no authentic cases of photochemical effects produced by electrical waves, the writer sees no reason why such reactions are impossible, and indeed there seems to be ground for believing that some instances of this kind will be discovered. It is reasonable to suppose that if certain systems are placed in a very powerful magnetic field so as to produce a condition of great stress or strain, the long electrical radiations might be able to produce changes in electronic configuration which would bring about chemical reaction.

The four principal fields of interest now occupying the mind and attention of the photo chemist are:

(*a*) The photo-equivalence law of Einstein and the Lewis-Perrin radiation hypothesis
(*b*) The production of cold light.
(*c*) The improvement of monochromatic light sources.
(*d*) The laboratory synthesis of carbohydrate and protein material by the instrumentality of light.

Radiation Hypothesis

The radiation hypothesis furnishes the present battle ground of most interest, and rightly so, because once we learn the ultimate relation between chemical activity and frequency, many of our other problems will at once be solved. During the progress of a fiercely contested battle it is not always wise to attempt to predict the final outcome, but it is now clear that the original form of the photochemical equivalence law of Einstein, based upon the quantum theory, is so rarely in accord with observed facts as to render it of little value in itself. Any law which has its sole foundation in the quantum theory of Planck is bound to be a subject for considerable dispute, inasmuch as this theory itself is by no means fully accepted by many physicists. To those who do not accept the quantum theory, the failure of the Einstein law and the radiation hypothesis of Lewis-Perrin is naturally the fulfilment of the expected.

Assuming the validity of the quantum theory, we soon find ourselves in other difficulties. The Einstein law is supposed to apply only to the *primary* light reaction, and the difficulty is that the total amount of reaction as measured may be not just the amount of primary reaction which takes place, but may be either greater or less than that amount, due to secondary reaction or reactions. It therefore becomes necessary to find a secondary reaction which is exactly equivalent to the primary one, since the latter can itself rarely be measured quantitatively. A substance which will react with the product of the primary reaction quantitatively so as to give a true measure of the primary reaction, is called an "acceptor," and the problem resolves itself into finding suitable acceptors for the reactions to be studied.

Fräulein Pusch[1] illuminated a mixture of bromine and hexahydrobenzene (the acceptor) and determined the extent of reaction from time to time. She then calculated the amount of bromine which should have been combined at these periods of time, using Einstein's law, and found a remarkable agreement between the observed and calculated values. Other acceptors, such as heptane, toluene, and hexane, were tried, but these gave too much bromine combined; on the other hand, hydrogen proved to be an unsuitable acceptor since the amount of bromine actually combined was only about one one-hundredth the amount required by the photo-equivalence law.

The Lewis-Perrin radiation hypothesis, while appearing to be somewhat more hopeful than the original formulation of Einstein, has been shown to have many weaknesses and, in fact, some apparently insuperable difficulties.

Our story starts back in 1889 when Arrhenius deduced a relation for the chemical reaction which has been and still is of considerable value, although the original theoretical basis for the relation has been shown to be unsound. Stated mathematically, this relation is

$$\frac{d \log k}{d T} = \frac{A}{T^2}$$

where k is the velocity constant of the chemical reaction, A is one-half of the energy required to change one molecule of inactive material to an active form, and T is the absolute temperature. According to this relation the temperature coefficient of chemical reaction should be diminished in a homogeneous system by an increase in concentration of the catalyst. Not only has this not been found to be true, but the actual existence of special activated molecules, such as Arrhenius postulated, seems a matter of much doubt. In 1914 Marcelin formulated a relation much the same as that of Arrhenius, which has the form

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[1] *Z. Electrochem.*, **24**, 335 (1918).

$$\frac{d \log k}{d T} = \frac{E}{R T^2}$$

E being defined as the "critical energy" which it is necessary that the molecule absorb, in addition to that already possessed, to render it active; and, following the suggestion of Lewis, this quantity has since been called the "critical increment." Somewhat later (1915) Rice deduced the more mathematically exact relation

$$\frac{d \log k}{d T} = \frac{V_c - V_m + 1/2\,(RT)}{R T^2}$$

Here, V_c is the critical value necessary before reaction takes place and V_m is the value of the mean potential energy of the molecules undergoing reaction. Next, Lewis and Perrin, independently, made the assumption that the source of the energy increment is infra-red radiation, and Lewis pointed out that this quantity should be determinable from the temperature coefficient. If, for example, we know the value of the velocity constant for a reaction at 25° C. and 35° C., we should have

$$\log \frac{k}{k} = \frac{E}{R}\left(\frac{1}{298} - \frac{1}{308}\right)$$

Taking the hydrolysis of methyl acetate as an example, the increase in k for 10° C. is 2.5. From the relation above, E is 16,800 calories per mol, or 1.03×10^{-12} ergs per molecule. By the photo-equivalence law of Einstein ($N = \frac{E}{h\nu}$, where h is Planck's constant, 6.547×10^{-27} erg second, ν the frequency, E the heat absorbed to produce the reaction, and N the number of molecules dissociated by light of frequency ν), Lewis finds that for the infra-red radiation $\lambda = 7.5\ \mu$, corresponding to the absorption band for methylacetate, $h\nu$ should be 0.262×10^{-12} ergs, or 4 $h\nu$ would furnish the quantity of energy E.

According to the radiation hypothesis of Lewis, catalytic reactions should be fully explained. The function of the catalyst, according to this hypothesis, is merely to absorb infra-red radiation of the proper wave length and pass it on to the reacting molecules.

According to this hypothesis, when reactions take place in solution there should be a definite absorption band for the solute, and the position of this band should be capable of calculation. The decomposition of triethylsulfine bromide in nitrobenzene has been studied by von Halban.[2] From his data H. A. Taylor, in Lewis' laboratory, calculated the critical increment E and found it to be 28,530 calories, which corresponds to a value of 3.0×10^{14} for ν or a wave length of 1.0 μ. Taylor then proceeded to determine the location of absorption bands for triethylsulfine bromide in the spectral region 0.8 to 3.1 μ, and found that there is but one distinct band in this region, a band appearing at 1.05 μ, which is very close to the value calculated from the critical increment. This excellent agreement is, however, a rather exceptional instance. In most cases where the hypothesis has been tested, the calculated and observed absorption bands do not at all coincide.

The application of the radiation hypothesis to monomolecular gas reactions should afford an interesting test of the value of the hypothesis. This has been accomplished by Daniels and Johnston[3] for the decomposition of nitrogen pentoxide. They calculated the critical increment and found it to be 24,700 calories. The wave length required for the decomposition of nitrogen pentoxide should therefore fall at 1.16 μ, but, unfortunately for the theory, this substance is not decomposed by radiation in this region of the spectrum. There is a marked absorption band at 5.81 μ and a less marked one at 3.39 μ. These values are about five and three times the required value of 1.16, respectively. The significance of this is not yet clear. Daniels and Lueck[4] have also investigated the decomposition of nitrogen pentoxide dissolved in various solvents. Here the agreement between experiment and theory is no better than for the case cited for the reaction in the gas phase.

Summarizing the situation, we may say that during the past three or four years much attention has been devoted to this interesting hypothesis—an hypothesis which would be of the utmost value if found to be substantiated. However, it must be frankly admitted that the present outlook for the hypothesis, at least in its present form, is not encouraging. It is quite possible that something fundamental is being overlooked and that eventually we may be able to deal with reactions in a satisfactorily quantitative manner. On the other hand, the fundamental postulates may be wrong.

PRODUCTION OF COLD LIGHT

This is a subject of great practical interest. Our modern lighting methods, in which visual radiation is produced by heating bodies to incandescence, are naturally very wasteful, since a large amount of energy is lost as temperature radiation. The firefly and glowworm have solved the problem somewhat better, though we humans would scarcely be satisfied with either of these lighting systems. The firefly produces substances which by oxidation produce light with little or no temperature radiation. We must at least admire his efficiency! What the firefly can do, man should be able to do, and far better. Undoubtedly, the time will come when light will be produced by controlled chemical reaction, and in a more economical way than by the systems now in use. In one direction considerable improvement may be made, at least. Little expert knowledge is now used in the selection of paints and wall coverings in room interiors. Much of the light now absorbed and wasted may be saved and used by reflection, simply by a proper choice of wall covering. In addition, there is the possibility of using materials in paints and on paper or other surfaces that will emit light for many hours after receiving illumination during the day. It is felt that, in spite of all the excellent work done on phosphorescent sulfides, considerable work must still be done before we have the knowledge we need. There is distinctly a great field for research along this line in the hope of developing more efficient phosphorescent materials than are now known. Certainly, such an illuminating system, consisting of a soft glow emanating from the walls of a room, would be ideal from many points of view. Such illumination would not only be restful to the eye, but would give possibilities of unique artistic effects.

IMPROVEMENT OF MONOCHROMATIC LIGHT SOURCES

The dependence of photochemical reaction on wave length (frequency) has already been mentioned. A moderate change in wave length may completely negative the effect desired. For example, oxygen may be changed to ozone or ozone to oxygen merely by a moderate change in wave length of the light illuminating the system. If unfiltered ultra-violet light from a quartz mercury-vapor lamp is used, the result will be an equilibrium between the ozone and oxygen, the position of which will be dependent upon the relative intensities of the two groups of wave lengths involved, and upon the temperature. Usually, photochemical reactions are sensitive to a comparatively narrow band in the spectrum. If a wide band is used, energy is therefore wasted, and an undesirable result may be produced. Now that light is playing an increasingly important role in the photosynthesis of many compounds, it becomes more important that sources of very intense monochromatic illumination be developed. The present practice is either to secure approximately monochromatic light by dispersion of light through a prism, letting the desired wave length fall upon a slit behind which the reacting system is placed, or by the use of filters designed to filter out the wave lengths not desired. In either case, the intensity of the resulting illuminating beam is not great, particularly if it is anywhere near monochromatic. In order that reactions may be carried out on anything like a commercial scale, better means of producing powerful, intense sources of such light must be developed.

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[2] *Z. phys Chem.*, **67**, 129 (1909).

[3] *J. Am. Chem. Soc.*, **43**, 72 (1921).

[4] *Ibid.*, **44**, 757 (1922).

Synthesis of Carbohydrate and Protein Material

Much interest has lately been aroused in the synthesis of carbohydrates and protein material, particularly as a result of the fine investigations of Baly and his co-workers in England and Baudisch in this country. As a result of these investigations the mechanisms of these photochemical processes are better understood, and while the work of the two groups is not entirely confirmatory, at least much progress has been made. It is believed that because nature seems to use chlorophyll for the synthesis of carbohydrates, it does not necessarily follow that this is the best of all possible catalysts, and it is the hope of the photo chemist that new and more effective catalysts may be found for this important photochemical process.

Utilization of Radiant Energy of Sun

Another photochemical problem of great interest, and one which has excited the imagination of the scientists of many generations, is the possible utilization of the enormous quantities of radiant energy coming from the sun. Waste places, now useless for any purpose, may eventually become the sites of great manufacturing plants, once the secret of transforming radiant energy into chemical energy is solved. Here we have an unlimited and almost constant source of energy of enormous magnitude, and one which by its successful utilization will tend to neutralize in a large measure the effect of our diminishing coal and oil supply. While the coal and oil problem may not be a serious one for the present generation, surely the time will come when other sources of energy supply must be found and utilized if civilization is not to perish. Knowing that hundreds of billions of horse power of radiant energy are constantly coming to the earth from the sun, it is not strange that the photo chemist casts a speculative eye toward the possible utilization of this enormous amount of energy, a very considerable portion of which is now entirely wasted.

Occurrence of Levo-Menthone in Pine Oil[1]

By Augustus H. Gill

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The pine oil known as "Apinol" was manufactured by dry distillation of wood, the heat being controlled by a circulating oil bath, the three fractions being turpentine, pine oil, and impure resin oils known as tar oils. This had been redistilled so as to free it from the turpentine fraction; it had stood for about fourteen years, giving ample opportunity for resinification. The physical characteristics of the sample were:

Specific Gravity at 15.5° C.	Refractive Index at 20° C.	Optical Rotation at 26° C.
0.9856	1.4868	−7° 20′

The oil was distilled under 4 mm. pressure, at first small quantities of water and terpenes distilled over, and a large portion, about 60 per cent, distilled over between 74° and 79° C. Fraction between 79° and 100° C. was 10 per cent.

By repeated fractional distillation of the first fraction at atmospheric pressure, two distinct fractions were isolated, one boiling at 202° to 203° C. which constituted 8 per cent of the original oil, while the other had a boiling point of 208.5° to 209.5° C. and constituted 20 per cent of the oil.

The fraction boiling between 79° to 100° C. at 4 mm. was gluey to the touch and was suspected to contain terpineol; attempts to convert it into terpin hydrate by the method of Tiemann and Schmidt[2] were in vain; hence, the oil contained no terpineol, thus differing in its most important constituent from the pine oils so far studied.

The fraction boiling at 202° to 203° C. was thought to be fenchyl alcohol. It was optically inactive. It was oxidized to its corresponding ketone fenchone by nitric acid.[3] The inactive fenchone thus obtained had a boiling point of 193° C. and an odor resembling camphor. The inactive fenchone was next converted into semicarbazone with semicarbazide hydrochloride, having a melting point of 173° C., differing from the active form which has a melting point of 182° to 183° C. Thus, the presence of inactive fenchyl alcohol was conclusively proved.

The second fraction, which was levo-rotatory, having an optical rotation −20° 28′, was identified as *l*-menthone by converting it into semicarbazone, melting point 184° C. This was the first time that *l*-menthone was isolated from oils of the Pinus family.

A study of the resinous matter in the oil was made by steam distilling the oil, when the first half, which distils over, contains all the fenchyl alcohol and *l*-menthone, and an appreciable quantity of resinous matter. The other half, which remains in the flask, consists of a viscid liquid, an examination of which showed an acid value of 2.7, saponification value of 17.2, and an iodine value to be 65.6. These values are in very close agreement with those found for rosin oil, except for the fact that the rosin oils so far studied are strongly dextro-rotatory, the value varying from 30 to 50, while this sample under examination was levo-rotatory, having a value of about −14°. It is possible that some of the menthone in the oil may have polymerized or resinified, thus giving a levo-rotation. It gave the Renard, Liebermann-Storch, and Halphen reactions for rosin oil.

This pine oil differs from others in its high menthone content and absence of terpineol; besides fenchyl alcohol it probably contains small quantities of terpenes and sesquiterpenes, which have changed into the resinous body, the remainder constituting a large percentage of the rosin oil, with small quantities of rosin spirit and colophony.

Acknowledgment is due M. J. Karasji by whom some of the work was performed.

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[1] Received July 10, 1923.

[2] *Ber.*, **28**, 1781 (1895).

[3] *Ann.*, **263**, 131, 146 (1891).

Research for the Petroleum Industry

By **Raymond F. Bacon**

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THERE is no industry of anything like the magnitude of the petroleum industry which has such a dearth of fundamental chemical knowledge on which to base its operations. The reasons for this fact are twofold. One is that petroleum refining as conducted in the past has been largely by physical separations rather than by chemical processes. The other is that a study of the structure and reactions of petroleum hydrocarbons involves very great difficulties. The industry in the past has separated the petroleum into certain of its original parts and has marketed these parts as gasoline, kerosene, lubricating oil, fuel oil, paraffin, etc. The time has now come when commercially successful petroleum refining means the manufacture from the oil of substances which do not exist in the crude petroleum as such, but are formed by chemical transmutations from other compounds present as constituents of the petroleum. For example, the time has come when not all the kerosene hydrocarbons which exist naturally in crude petroleum can be advantageously sold as kerosene. Ideal refining means production from the crude oil of only those products which can be most profitably marketed at a particular time. This means chemical change of many of the compounds contained in petroleum into other chemical individuals.

Bachrach

RAYMOND F. BACON

The industry is meeting this situation, as the thousand and more patents relating to cracking processes for making gasoline would indicate. The industry, however, could work out its salvation much faster and on sounder lines if more were known regarding the nature and properties of the individual hydrocarbons constituting petroleum. One can read in scientific literature pages and pages describing the properties and chemical reactions of hydrocarbons of which at most a few hundred grams may have existed in the whole world, while tons and thousands of tons of hydrocarbons are being produced daily of which we know absolutely nothing regarding their chemical properties, their reactions, and their structure. There is almost no field of research open to the pure scientist which offers such fascination in its difficulty, nor such promise, if its difficulties are overcome, of opening up a whole new field of chemistry, as the study of these unknown petroleum hydrocarbons. The action of heat alone on these hydrocarbons, under all possible conditions, is an alluring field of study, and on this heat action (pyrolysis) most of the processes of gasoline manufacture are founded, but largely on an empirical basis. As an example of interesting relations of this character, the Burton and other similar pressure distillation processes of cracking give gasoline which, considering its saturated constituents,[1] is apparently of much the same character as the gasoline hydrocarbons found naturally occurring in petroleums. On the other hand, when heavy petroleum oils are cracked under the conditions of the Ramage process, the gasoline hydrocarbons obtained have for similar boiling points a much higher specific gravity and a much higher refractive index, indicating that the hydrocarbons formed are probably ring compounds. Still, so far as the writer's observation goes, these ring compounds formed in this way are not of the same character as the naphthenes, as they do not show the same resistance toward chemical agents as the true naphthenes.

ELECTRICAL WAVES IN CRACKING PROCESSES

In the patent literature on cracking processes claims are made by various inventors of the efficacy of electrical waves, of the impact of ions, and even of mechanical impact itself in causing the breaking down of hydrocarbons containing many carbon atoms into those containing a lesser number. Scientific workers would find here an interesting and perhaps profitable field of investigation, for it is, of course, known that under proper conditions electrical waves of suitable character can cause profound changes in chemical compounds. It is also known that electrons meeting molecules at sufficient velocity can cause the disintegration of those molecules, thus forming new compounds. Furthermore, impact of sufficiently violent character does cause the breaking down of many types of compounds—as, for instance, explosives. The scientific study of reactions of this type should yield most valuable results which might also possibly prove to be of great practical value.

LUBRICATION

When one considers the subject in all its ramifications, there is hardly anything in the world quite so important as lubrication. The world's consumption of lubricants does not rank with its consumption of many other products, but without the lubricants all machinery stops. There is no doubt that one of the greatest sources of worry of the German General Staff in the war was as to whether they could maintain a sufficient supply of lubricants in a shut-in Germany. Yet, with the subject so important, what do we know about the scientific nature of lubrication or the chemical or physical structure of a substance which makes it a good lubricant? Our ignorance is really appalling. The writer well remembers the fascination with which he heard Dr. Mabery tell about how he had fractioned a certain petroleum into various narrow fractions and had found that one of these fractions made a most excellent oil for lubricating watches, while a nearby fraction was of such a character that it stopped the watch. It is well known to all who are conversant with the subject that there are no chemical or physical tests which can be made on a new product which will prove definitely whether or not it will serve as a good lubricant for a particular piece of machinery. The only test that is of real value is to try it on the machine to be lubricated.

In this connection, there is another subject which offers great promise for investigation, and that is the relation of those hydrocarbons which go to make up what we call "petrolatum" to other hydrocarbons, possibly with the same number of carbon atoms, which are either liquid oils or are solid, crystalline compounds of the type which make up paraffin wax. There are indications that in petroleum there may be at least three classes of hydrocarbons all with the same number of carbon atoms, one class being liquid at ordinary temperatures, another of the consistency of petroleum jelly, and still another solid and of crystalline structure at ordinary temperatures. A joint attack on a problem of this kind by men with the viewpoint of the colloidal chemist and of the structural organic chemist would seem to promise greatest results.

Before leaving the subject of lubricants it should be pointed out that there are many indications that small quantities of other substances mixed with the base lubricant may greatly improve the qualities of that lubricant. In fact, from the viewpoint of those who think in matters colloidal, it may be that a good lubricant is a colloidal dispersion of a substance in a liquid which itself may have only indifferent lubricating qualities. In this connection, it might be mentioned that it has been well proved that one requisite of a good lubricant is that the lubricant should stick tightly to the metal surface lubricated; it should, in other words, so tightly adhere to the lubricated surface that it is almost impossible to remove every trace of it. The process of the flotation of ores is based on the fact that certain kinds of substances preferentially wet metallic or metal-like mineral surfaces as compared to gangue surfaces. The quantity of substance required to change the surface sufficiently to permit the flotation of ores is extremely minute, and there is every reason to believe that there is an actual adsorption of the flotation agent on the metallic surface. Substances of very diverse chemical and physical properties exhibit this phenomena, such as fatty oils, petroleum oils, phenol and cresol, and even soluble solids like α-naphthylamine and thiocarbanalide. May it not be that small quantities of properly chosen materials colloidally disbursed in the usual lubricating oils might increase this wetting or adhering power of the lubricating surface and thus make better lubricants? This subject has its fascination not only from the industrial possibilities, but also from the pure science standpoint. The reason why one liquid will wet a certain surface and another will not is one of the very obscure phenomena of physical science, and it is only recently, since Langmuir and others have visualized the actual physical structure of the molecules, that any picture at all has come to us as to why or how these things can be.

Utilization of Natural Gas

One of the great problems of the petroleum industry is the utilization of natural gas. In almost all new petroleum fields large quantities of natural gas are found in the wells. Wells flowing 10,000,000 feet of natural gas per day are not unusual and those with 50,000,000 feet have been recorded. The petroleum field is usually located so far from industrial centers that this gas cannot be profitably piped for fuel purposes. Moreover many structures drilled for oil yield little or no oil, but large quantities of natural gas. If this natural gas contains small quantities of the higher hydrocarbons, it is usually stripped of these hydrocarbons, which form the so-called casinghead gasoline of commerce. The methods in use for obtaining casinghead gasoline from natural gas are fairly satisfactory, but one great need is to so simplify the apparatus that it can be cheaply moved when the gas supply diminishes. The stripped gas is used to a minor extent in drilling operations and in local industries, but the history of most fields is that a great percentage of it escapes and is wasted. Natural gas is utilized in some fields for the making of carbon black, and this is quite justifiable at points where no better use can be made of the gas. Carbon black is an important and necessary commodity, the use of which is rapidly increasing. The attack on the use of natural gas for carbon black manufacture is based on the fact that the gas by present methods only yields 1 or 2 pounds of carbon black per 1000 cubic feet of gas consumed, whereas the gas actually contains upward of 40 pounds of carbon black for each 1000 cubic feet. Researches directed toward increasing the percentage of good carbon black obtainable from natural gas offer a field alluring both from the industrial and from the pure science standpoint. If natural gas is subjected to sufficiently high temperature, it is completely broken down into carbon and hydrogen, and in that case the yield of carbon obtained is about 40 pounds per 1000 cubic feet of gas. The carbon obtained in this way has a relatively high specific gravity, is grayish in color, and is somewhat gritty, instead of having the low specific gravity, the desirable velvety black color, and freedom from grit demanded of commercial carbon black. In the operations for the manufacture of casinghead gasoline from natural gas, the casinghead gasoline obtained usually contains very considerable percentages of the lower members of the paraffin series of hydrocarbons, particularly the propanes, butanes, and pentanes. These very low boiling hydrocarbons are allowed to distil from the casinghead gasoline either in special apparatus designed for the purpose, or very often by a simple process of weathering. They offer a cheap raw material for the synthesis of many classes of compounds containing three, four, or five carbon atoms, and the amount of such material available is sufficient to supply a very large industry.

Treatment of Distillates

It is the practice of the petroleum industry to treat various distillates with acid and alkali for the purpose of removing the color and certain undesirable constituents and improving the odor. In this treatment the acid that is virtually always employed is a strong sulfuric acid, and in the case of most gasoline and burning oil distillates the refining loss from such treatment is rather small. In the case of the higher boiling oils, such as lubricating oils, the treatment loss is often very considerable, so that the study of methods of "treating" higher boiling petroleum distillates is a subject very worthy of investigation. Sulfuric acid probably acts in two ways in the treatment of petroleum distillate. It acts chemically on certain unsaturated hydrocarbons, polymerizing them, and it also acts physically as a solvent for some of these polymerized tars and for certain other tarry or nitrogenous materials which are in the oil. Very often its action may go too far and compounds are formed which are of an emulsifying nature and which render separation of the oil from the alkali or from water, a subsequent operation, very difficult. Similarly, treatment for the refining of cracked gasoline also is apt to cause heavy refining loss. It used to be thought that the treatment with acid in any case was for the purpose of removing unsaturated hydrocarbons, and that unless these unsaturated hydrocarbons were removed the distillate would after a certain length of time lose its color, take on offensive odors, and in many cases separate gummy matter. It has been shown that it is not the unsaturated hydrocarbons *per se* which cause these phenomena, although when certain other objectionable substances are present reactions are started in which the unsaturated hydrocarbons probably take part and probably do cause part of the phenomena mentioned. There is, however, good reason to believe that the removal of only exceedingly small amounts of the offending materials from any petroleum distillate will give a product of proper color and of sufficiently good keeping qualities for commercial purposes, and that the present large refining losses on certain petroleum distillates are unnecessary. The problem is to find cheap commercial methods of reaching this ideal.

Possibilities of Industry

The problems which have been mentioned are those which are intimately connected with the present practical operation of the industry and are, in the writer's opinion, problems of a character for which a satisfactory solution can be found. In addition, there is an immense field of problems whose solution is more chimerical. We have all heard the petroleum industry compared with the coal-tar industry and the belief that some day there will be a great organic chemistry of the petroleum products, the same as there is a great organic chemistry of the coal-tar products. The budding young organic chemist should be reminded that the reputations of most of the great organic chemists of the last century were based on the solution of problems connected with products from coal tar and that the time will come when some new Baeyer will open up the chemistry of petroleum products. It will probably be many, many years, however, before real progress has been made in systematically ordering and arranging the reactions of chemical compounds derived from petroleum. Nevertheless there are certain fields along these lines which appear somewhat less difficult than some of the others and which have great industrial importance. One is the manufacture of resins from petroleum. Fossil resins are rapidly being exhausted. Certain synthetic resins of the type of Bakelite are almost ideally adapted for various industrial uses, but resins of this type are necessarily somewhat high in price and cannot be used for all purposes. The coumarone resins, prepared by polymerization of certain liquid fractions from coal tar, are supplying a certain need for lower priced material, but there is still a big field, especially in light-colored, durable resins to be prepared from fractions of petroleum. The writer believes that this will be done within the next few years.

Another similar field which offers promise is the preparation of true drying oils from petroleum. The drying oils are characterized by containing certain double bonds which in drying absorb oxygen, making the hard elastic film demanded by the paint industry. In other fields of chemistry it is possible to put double bonds into compounds at will, and there is little doubt that properly directed work could ascertain how to do this in the field of petroleum hydrocarbons.

Another field is the manufacture of acids from the higher petroleum hydrocarbons, it being assumed that such acids would be suitable for the manufacture of soaps. Much work has been done on this subject, so far without any commercial success. It is probable that this problem is a much more difficult one than those mentioned previously.

The solution of chemical problems of this character will be a benefit, not only to the industry itself, but to the great general public along the lines of conservation. Our descendants will, no doubt, be shocked that the people of this generation burned as fuel oil useful hydrocarbons from which they will know how to manufacture many very valuable and necessary materials; but the use of certain fractions of petroleum for fuel is justifiable at the present time because we know of no better utilization of this material. Workers in pure science can find no field of investigation offering more promise from the purely scientific standpoint, nor from the standpoint of benefiting industry and their fellow men, than in taking up some of these problems of the great petroleum industry.

Radiator for Platinum Crucibles[1]

By Manuel M. Green

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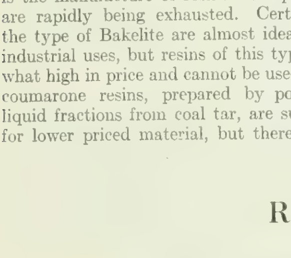
A SHORT time ago while carrying out an investigation on the determination of potash in acid-insoluble silicates,[2] the writer decomposed the samples with hydrofluoric and perchloric acids, at first evaporating the solutions of perchloric acid fumes by hand. Owing to the fact that there was some loss by spattering, the type of radiator made of sheet iron recommended by the Geological Survey[3] was used. For such a radiator, when a platinum bottom is not used, it is necessary to use the full heat of a Tirrill burner, or else a Méker burner. As the investigation was carried out during the summer months, the discomfort accompanying the continuous use of so large a flame led to a search for a more comfortable means of getting the desired result.



Thornton[4] recommends the use of a 100-cc. nickel crucible for a radiator, claiming that only a small flame is needed to heat the platinum crucible uniformly. While Thornton's apparatus is more desirable than the other, it was deemed advisable to improve on it if possible, and the following piece of apparatus was constructed to replace the older type.

A piece of wire gauze, 12.5 cm. square, is bent into the capsule shape indicated in the diagram, by simply hammering the center, *A*, of the gauze, supported on a metal knob, as far in as it will go, then bending back the corners, *B*, so as to provide a means of suspending the apparatus on a ring stand. From a second piece of gauze a round piece, *C*, is cut of such a size that when fitted into the first part it is held about 2 cm. above the center, *A*. A triangle, *D*, is next fitted in 1.5 cm. above *C*. The triangle *D* may be made from an ordinary chromel triangle used in ignitions by cutting off all the curled part at the corners with the exception of just enough to keep the triangle together.

If, now, the crucible containing the solution to be evaporated is placed in the triangle, the bottom of the crucible comes about 0.5 cm. from the bottom *C*. A very small flame, the smallest obtainable from a Tirrill burner without having it go out, if directed at point *A* (the apparatus being supported so that the tip of *A* comes about 3 cm. above the tip of the flame), causes the solution to evaporate rapidly and smoothly, without spattering, to fumes or dryness as desired.

This new type of radiator has the advantage over the older types in economy of heat, economy and ease of construction, and elimination of discomfort.

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[1] Received August 3, 1923

[2] This Journal, **15**, 163 (1923).

[3] Hillebrand, "Analysis of Silicate and Carbonate Rocks," *U. S. Geol. Survey, Bull.* **700**, p. 33.

[4] This Journal, **3**, 419 (1911)

The Paper Industry: Problems and Recent Developments

By Bjarne Johnsen

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WHEN wood was introduced as a paper-making material, about the middle of the 19th century, it was believed that an inexhaustible supply of raw material had been found. It is true that there are sufficient areas available to produce all wood necessary, but experience has shown that only a very few countries have realized the importance of assisting nature in maintaining the forests. These countries have conserved their supplies by forest management, other countries have kept their supplies by importing wood, and still others have depleted their supplies and are now anxiously looking for new sources either of wood or other materials. Hand in hand with the depletion of the forests of the world a very rapid increase in consumption of paper has taken place, and the most important problem for all paper-producing countries is now conservation of existing forests and development of new forests by reforestation. While the paper industry uses only a small percentage of the total wood consumed, the paper manufacturers, either directly or through various associations, are doing more toward conserving and improving forests than any other wood-using industry.

Bjarne Johnsen

With the tremendous increase in the manufacture and consumption of paper, wood supplies have to be secured from greater and greater distances from established mills, which results in increases in costs due to freight charges. As a result of the increased costs of raw materials the mills are directing their attention more and more to improvements in processes leading to greater efficiency and economy.

The yield of mechanical and chemical pulps has been materially increased by the introduction of barking equipment, which permits the removal of bark without at the same time removing part of the wood, as was the case with the knife barkers which previously had been universally used.

In the chemical cooking processes efforts are now being made to increase yields by improvements in existing methods and by development of new methods. In the manufacture of soda and sulfate pulps it has been found that impregnating wood chips with cooking liquor at a low temperature and then drawing off the liquor and steaming results in a considerable increase in the yield of pulp. This idea originated several years ago with the sulfite process in which, however, it has not so far been a commercial success, owing to the fact that complete impregnation of chips with the bisulfite solution is very difficult to accomplish. However, it is claimed that the yield in the sulfite process can be appreciably increased by heating the chips with water or waste liquor from previous cooks before actual cooking is started. By the addition of sulfur to the alkaline cooking liquors it is claimed that higher yields and better quality of fiber can be obtained in a shorter cooking time.

Improvements in Sulfite Process

Experiments with the use of sodium sulfite in place of calcium bisulfite have recently been continued, with very promising results as far as yield and bleaching quality of the product are concerned. The main problem connected with this process (Bradley and McKeefe) when operated on a commercial scale is the recovery of the sodium salt which is necessary to make the method economical. It is anticipated that the application of sodium sulfite will make possible the utilization of certain woods which cannot be successfully cooked with calcium bisulfite.

A higher yield and better quality of fiber, as well as a saving in fuel and chemicals, are claimed by the use of a patented modification of the sulfite method (Decker), in which the relief gases and liquor are transferred from one digester to another during the cooking operation. It is reported that this method has been successfully operated in a Canadian mill for some time.

Resinous woods, such as the southern pines of the United States, have not been utilized in the sulfite process without previous extraction to remove the pitch. Recent reports from Europe discourage the use of organic solvents for this purpose but encourage treatment with weak solutions of alkali previous to sulfite cooking. In some newsprint mills jack pine has been handled without previous extraction by the sulfite process with fairly good results, and investigations are under way to find out if high grade sulfite pulp can be produced from this raw material, which is quite plentiful in Canada.

The greatest progress in the improvement of existing methods, particularly in the sulfite process, has been accomplished as the result of increased knowledge of the chemistry of wood and the chemistry of the reactions which take place during cooking. Investigations along these lines which are being conducted by scientific institutions as well as by various mills will undoubtedly result in further improvements in the near future.

Recovery of By-products

A great problem in the refinement of the pulping methods is the recovery of by-products. In spite of the numerous methods which have been proposed for the utilization of the organic matters contained in sulfite waste liquor, the problem cannot be considered as solved. A large number of the plants which have been recently erected, particularly in Europe, for the production of ethyl alcohol, some of which were in operation during the war period, have now discontinued operation. This has been due partly to adverse legislation and partly to competition with other materials because of the higher cost of production of ethyl alcohol from this waste. Other products have been produced commercially in some countries for use as substitutes during the period of abnormal market conditions. With the improvement in the design of evaporators it has been found profitable in some cases to use the concentrated liquor as a fuel, but this should be considered rather as a destructive disposal of the liquor in locations where its elimination has been found to be necessary. The real problem will not be solved until it is possible to separate the various constituents of the liquor and refine them into high-grade products.

In the alkaline processes it is customary to evaporate the waste liquors in order to recover the alkali, in which case the organic matter furnishes the fuel necessary for incineration. A recently developed process (Rinman) which has already been commercially used with success, includes the recovery, from the organic matters, of methanol, acetone, and various oils by means of distillation, and in this case the fuel gases developed in the process are used for heating the retort.

Along the line of conservation of wood are the attempts to develop better ways of storing pulpwood so as to reduce losses due to decay. Investigations have been made to throw more light on the actual losses and the effect on the quality of fiber as a result of decay. Valuable work is also being done to determine the most profitable ways of utilizing wood which has decayed in the standing forest or during the storage period.

WOOD SUBSTITUTES

While wood is the ideal raw material for the ever increasing production of paper, a certain amount of the fiber required is being secured from other sources, such as various straws and grasses. Esparto and straw are extensively used in Europe for the production of high-grade papers, and investigations are constantly being made to determine the value of other plants, such as bamboo, reeds, various grasses, and the like. The use of these raw materials has not been considered very attractive in countries where wood could be easily obtained, because of the difficulties in harvesting, transporting, and storing of materials of such a bulky nature, and also on account of lack of uniformity in the materials which makes the application of existing processes difficult. Nevertheless, it is reported that a mill is in operation in Florida for the purpose of utilizing saw-grass for the manufacture of high-grade pulp. In spite of the difficulties in harvesting and the low yield, this mill is planned for an ultimate production of 100 tons a day.

Investigations so far seem to point to the desirability of handling these plant materials by a combination of cooking processes with utilization of by-products, which results in greater economy, a better product, and higher yields. Such results are claimed for chlorination processes (DeVains, Peterson, Cataldi, etc.) recently developed in Europe, which include treatment with weak alkali followed by a chlorination either with the chlorine gas or in aqueous solution. After the chlorinated substances have been removed by means of weak alkali, a yellow product is obtained which can be refined to a white pulp by means of the ordinary bleaching process. It is pointed out that such a process is particularly attractive in localities where power is cheap, because sodium chloride and lime are the only chemicals required.

IMPROVEMENTS IN BLEACHING

In the bleaching process improvements in equipment make it possible to bleach at a high density and a low temperature, which results in a saving of bleach and an increase in yield. Such equipment has been developed more on the basis of experience than as the result of scientific research. It is only very recently that Schwalbe published results of extensive investigations on the bleaching of pulp, which not only explain many of the practical experiences, but also give additional information regarding the chemistry of the process. This information will undoubtedly influence future development of bleaching equipment. A very interesting result of his experiments is the establishment of the fact that during bleaching carbon dioxide is developed which is absorbed by the fiber and retards the bleaching. This shows the necessity of removing the carbon dioxide by mechanical means, such as agitation, or by increasing the temperature.

Another important result is the difference in the action of chlorine and hypochlorous acid because of their effect on yield and on the final purity of the fiber, the hypochlorous acid reacting with the coloring matters while the chlorine attacks residual lignin compounds. Similar conclusions were reached by Heuser and explain results obtained by investigators who have studied the comparative merits of acid and of alkaline bleaching and the effect of a combination of both.

SIZING

Probably the most important chemical operation in the paper mill is sizing. There has been much discussion concerning this process and much difference of opinion concerning the chemistry of the operation. During the past year independent investigations by Heuser, Lorenz, and Sieber have reached practically the same conclusions—i. e., that the sizing is the result of several distinct reactions, the most important of which are adsorption between the two colloids, free rosin and aluminium hydrate, and a further adsorption of the compound thus formed by the colloidal cellulose fiber, the reactions being based on the electric charges of the respective substances. In these reactions the importance of the application of colloid chemistry is, perhaps, more clearly demonstrated than in any other papermaking process. Further steps in the investigation of sizing must include consideration of the colloidal nature of the cellulose fiber to a greater extent than has been the case heretofore. There must also be included a more thorough study of the colloidal changes of the cellulose fiber as affected by the beating process. The economy of the beating process, so far as beater construction is concerned, can be successfully studied on the basis of the excellent contributions on this subject recently made by Sigurd Smith.

IMPORTANCE OF SCIENTIFIC CONTROL

Many of the developments which have been mentioned are the results of investigations carried out in scientific institutions. In order to apply such results to the best advantage, the services of technically trained men are necessary and the tremendous improvements which have already been made in the efficiency and economy of the processes, as well as in the quality of the final products, are due to a large extent to the wider employment of technically trained men. While technical control is by no means universal, there has been a decided improvement in this respect during the past few years, and there is an increasing tendency on the part of even the smaller mills to follow the example of the larger companies which have successfully applied strict scientific control to all their operations and products. As one example of the result of control it may be pointed out that only a very few years ago it was considered impossible to increase the speed of newsprint machines to 1000 feet per minute. To-day there are machines running at even greater rate and other machines are under construction which are expected to operate at much higher speeds. This development is, of course, due to a large extent to the mechanical improvements in paper-machine construction, but no less due to the uniformity of the ground wood pulp, which is a direct result of scientific control of the grinding process. This illustration of the results of scientific control in the comparatively simple newsprint process indicates what is being done and what can be accomplished in the more complicated operations involved in the manufacture of finer papers.

The economic utilization of fibrous raw materials also includes prevention of losses. In the course of the manufacture of paper there are a number of washing and concentrating processes in which the waste waters may carry away large amounts of fibers. The reduction or elimination of these losses, which in some mills are very large, is one of the problems of a special committee of the Technical Association of the American Pulp and Paper Industry. So far the work of this committee has consisted in finding out the nature and amount of these wastes and in informing mills which have neglected this subject how such losses can be determined, and also in investigating the most efficient equipment for recovery of this material. Most complete recovery has always been obtained by means of settling tanks or basins of various constructions, provided these are of ample capacity, and recently various coagulants have been suggested as a means of accelerating such settling. Another phase of the work of the committee is the utilization of wood room refuse, such as bark and sawdust. These materials are commonly disposed of as power plant fuel, but since their fuel value is very low because of the large amount of moisture they contain, the efficient removal of the greatest possible part of the moisture by means of presses is being studied.

In the discussion of sizing and beating reference was made to the importance of a more exact knowledge of the part which the cellulose fiber, as a colloid, plays in the reactions. In the other processes, such as cooking, bleaching, dyeing, and the like, the value of a thorough understanding of the nature of cellulose is no less apparent. The establishment of cellulose research institutions in Europe and the United States and, more recently, the formation of a cellulose division of the AMERICAN CHEMICAL SOCIETY, is therefore keenly appreciated by the paper industry. More fundamental data concerning the material of prime importance, cellulose, which will be the result of further research must necessarily contribute more than anything else toward the development of the paper industry on a sound scientific basis.

Furnace Settings and Refractory Cements

By **F. J. Wakem**

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MOST manufacturers underestimate the importance of furnace settings. With economy in view they instal modern equipment and conveniences and then counteract this economy by paying little or no attention to the heart of their production—combustion chambers. A little thought and consideration can in most cases prevent furnace failures, which mean holding up of production, idle labor, and costly repairs.

The purpose of furnace settings is to provide a chamber for the most efficient combustion of the fuel used which will in the best manner possible direct the heat to the absorbing surfaces without waste and without the intermingling of excess air. Naturally, the most economical results are obtained when these settings stand up without impaired efficiency under the conditions incidental to their service for the longest possible time. While oil burners, mechanical stokers, and mechanical draft all contribute to increase plant efficiency, they result in more severe furnace conditions. Unless careful thought is given to the subject and the correct precautions taken, modern practice with its forced draft and other devices will result in frequent failures in furnace settings.

The design of furnaces varies so greatly with the different types, operating conditions, fuels, etc., that no general statement can be made to apply to all. Each individual case must be treated as a separate problem and the value of experience accepted. It is sufficient to say that the design of a furnace is of the utmost importance, for no manner of brickwork will stand up under faulty furnace design.

The different conditions require fire brick of varied properties; in certain cases, the choice of brick depends upon the heat-resisting quality; in others, resistance to the impinging action of the flame and spawling; while in others, upon the ability to resist the action of clinkers, slagging, and slice bar.

Two bricks may show up equally as well under a heat test of short duration, yet the one after a few weeks of hard service will change so that its thermal capacity is lowered, while the other will be practically unaffected.

The life of a furnace setting does not depend entirely upon the quality or type of brick used. Failures are often due to the inability of the fire clay or bonding cement used to fulfil its function. The best furnace setting has the proper design, is constructed by careful and experienced workmen, and is made of the best fire brick for the condition, bonded together and protected with a high-grade refractory cement.

Aside from the human element or workmanship, failures can generally be traced to one or more of the following causes: plastic deformation, spawling, cracking or bulging, clinkering, melting or slagging.

PLASTIC DEFORMATION

Plastic deformation or loss in compressive strength due to softening of the brick depends on the heat and load. If only one face or surface of a brick is exposed to the heat, the temperature may be increased to a point far beyond what the brick would stand if the entire brick were surrounded by heat or if even small portions of the other five surfaces were exposed. The reason is that when only one face or surface is exposed, the brick conducts the heat from that surface only. Exposure of the four adjacent surfaces of the brick to the face occurs in a furnace setting in which the fire clay or inferior cement bond between the brick has given away. This results from the melting out of the bond on account of its inability to resist the heat, or from the crumbling and falling away of the bond due to its failure to withstand expansion and contraction.

By using a good grade of bonding, refractory cement which will withstand the temperature without melting and which will not disintegrate and fall out of the joint when the brickwork is under stress, the flame can attack the brick on only one face.

Melting

Ordinarily, the fusion point of a fire brick would appear to be its most important characteristic, but in most cases failures will occur from plastic deformation before fusion occurs.

The same precautions as used in the case of plastic deformation will help materially to prevent melting of the fire brick.

Spawling

When expansion or shrinkage occurs within a short temperature range, if the change in volume is considerable or the temperature unevenly distributed, then failure by spawling is apt to occur. If more than one surface of the brick is exposed to the heat, especially portions of the four adjacent sides, that part of the brick which is so exposed becomes hotter than the balance of the brick and this causes internal stresses which result in spawling. Bricks adequately protected with a good refractory cement do not take on or give up heat so quickly as exposed brick, so the temperature range of expansion and contraction is increased. Besides, as the heat enters the brick from one face only, the temperature gradient is even and there is less probability of internal stress.

If spawling occurs or plastic deformation takes place, even though the bricks are bonded together with a suitable refractory cement, additional protection can be had by applying a $^1/_4$ to $^1/_2$-inch coating of super-refractory cement to the surface of the combustion chamber. The refractory cement used must have a high melting point, be dense, and have practically no shrinkage.

Cracking and Bulging

Expansion or contraction of fire brick will cause a setting to crack or bulge. When fire clay is used for setting up the brick, attempts are often made to overcome its inability to stay in the joint, by reducing the thickness of bond. This method throws all the stress due to expansion and contraction on the brick itself and causes more severe cracking or bulging. High-grade refractory cements have the necessary amount of elasticity to cushion this strain.

Slagging

The erosive action or slagging of fire brick by molten ash is very prevalent where coals are used, the ash of which softens at a comparatively low temperature. The flames carry particles of molten ash which enter the cracks or pores in the brickwork. This combination of ash and fire brick has a lower melting point than the fire brick itself. The deeper the molten ash enters the brickwork, the more severe will be the action. If the joints of the settings are well protected with a good bond, and the pores and minor cracks in the firebrick filled with a refractory cement applied as a wash coating, this slagging is less likely to occur.

Clinkering

It is practically impossible to prevent clinkering, but it can be retarded if the setting is made as smooth as possible. This can be accomplished by using a good bonding cement and then wash-coating the entire setting with a fine, high temperature cement designed for this purpose. The greatest trouble occurs in removing the clinker. Unless the fire bricks are strongly bonded together, which is not the case when fire clay is used, bricks are apt to be pulled out with the clinker. When parts of fire brick or even whole bricks have been pulled out of the setting with the clinker, the setting can be readily patched with a suitable high temperature cement.

Arches

A great deal of trouble is experienced with arches where replacement is difficult. Excess expansion or contraction and spawling give the most trouble. Arches bonded with a good refractory which hold the brick in place, cushion the effect of expansion and contraction, and protect the brick from spawling, will give better service. Suspended arches are rather expensive, but they are dependable, and separate bricks which have failed can be replaced with a minimum of time and cost.

Cements

Whenever possible it is preferable to use a dry, high temperature cement rather than a plastic cement, not only from a standpoint of economy, for plastic cements contain a large percentage of water, but also because of greater satisfaction in the results obtained. Plastic cements contain large quantities of fluxes, such as silicate of soda, which increase shrinkage and lower the fusion point of the cement. A high-grade, machine-mixed, dry, refractory cement will prove most economical.

When preparing dry refractory cements for use as a bond between the brick, sufficient water should be added to bring the mixture to the proper mortar consistency, which depends on the porosity of the brick. An excess of water should be avoided, and the mortar should be thoroughly mixed and free from lumps. The mortar should be battered or troweled on the brick already in place, the brick set on top and tapped until the joint between the brick is about $^3/_{16}$ inch thick and cement squeezes out between the edges. Instead of cutting off this cement that squeezes out between the brick, it should be plastered back over the face of the joint and brick so that it protects the edges. In other words a T-joint construction is recommended.

When using refractory cements for wash-coating, the cement should be thoroughly mixed with sufficient water to bring it to a thin grout consistency and then applied to the face of the brickwork with a stiff brush or broom.

In treating a fire box with a plaster coating of a super-refractory cement to resist spawling, plastic deformation, and melting, all clinkers and loose pieces should be removed, glazed surfaces chipped away, and sufficient notches cut in the wall to provide a key for the cement. The cement should be mixed to a stiff consistency and plastered over the setting to a depth of from $^1/_4$ to $^1/_2$ inch, depending on the condition.

One refractory cement cannot be a panacea for all ills. Conditions are so varied and requirements of a refractory so diversified that it is necessary to have different cements with different properties. Guesswork or haphazard treatment of refractory cement problems will mean early failure and expense that could be avoided. It is safer to realize the importance of using the correct material in the correct manner and call on the refractory manufacturer who has trained engineers available for this service.

Hammermill Paper Company Fellowships

The Hammermill Paper Company has offered a fellowship to Yale University for the purpose of developing a research work on cellulose chemistry. The recipient of this fellowship is John L. Parsons, and he will work under Dr. Hibbert during the coming year.

Another fellowship has been granted to the New York State College of Forestry to aid this institution in the development of a course in pulp and paper manufacture. Burton L. Kassing, who graduated this summer, will work for another year under the direction of Professors Wise and Libby on some fundamental work in connection with pulp and paper making.

The Trend of Research in the Nonferrous Industry

By **Paul D. Merica**

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TO ANYONE familiar with the nonferrous industries the title of this article will probably appear a highly idealized one. In the first place, the components of this industry—the aluminium, the copper, the zinc, the white metals, the nickel and cobalt, the brass rolling mill, the brass foundry, the die-casting industries—are, many of them at least, widely separated in interests, in uses, and in production methods, and it appears by courtesy only that we thus speak of a nonferrous industry.

It may also seem difficult at first thought to conceive of this composite group, each one of which is actually day by day wrestling with its own peculiar problems, as exhibiting any definite "trend of research" activities whatever. The term seems to infer a greater degree of group consciousness than actually exists. However, curiously enough, some major problems do appear to be common to most members of the industry and with which each is vitally concerned, and in this sense such a trend may be discerned; it is perhaps a statistical and not a conscious one.

It is pleasant to be able to record the fact that research is very definitely establishing itself to-day in practically all the nonferrous groups as a major element of industrial organizations. This realization may well be regarded as the consummation of a development which has taken place within the past twenty to twenty-five years—namely, the gradual assumption of administrative authority by men of engineering and technical training.

Twenty-five years ago, for example, the greater part of the copper refining in this country was done on the Atlantic seaboard, where coal and coke were to be had. The operating personnel was drawn from practical Welsh refiners, who at that time were considered to know everything which was worth knowing about the art. Copper they could produce, but it remained for the young technical graduates, entirely ignorant of it at the time, actually to advance the art of copper refining.

The influence of these men and of later ones like them is being felt in ever increasing strength; their word to-day even penetrates to boards of directors, and, if I hear it correctly it is this: You cannot continue to produce your (metal) products to-day, and—what is more important—you cannot continue to sell them in competition, except you have more and still more accurate information concerning them.

It is in the clearly evident response to this call throughout the nonferrous metal industries that the most clearly defined trend within them is seen. Research activity is here to stay; it is not a luxury, it is recognized to be a necessity. Individual companies are equipping themselves in every way to learn, both in physical and in human equipment. The amount of engineering and scientific thought now applied to these industries is probably fifty times as great as in 1900 and ten times as great as in 1912. A recent survey revealed the fact that over sixty manufacturers within the nonferrous industries maintained research departments and laboratories in 1920, in addition to the numerous control and operating technical personnel attached to many more smaller companies, principally foundries.

Parallel with the increased use of accurate thought and knowledge in these industries is developing also the increased use of new and better tools for aiding and testing production, a few years ago hardly known in the metal trades. The use of pyrometers is increasing rapidly in all branches, as well as that of testing instruments of all sorts—particularly, however, the microscope, which is, after all, responsible for some of the impetus which has been given to the research spirit of these industries in the past twenty-five years.

Well-defined standards for products are also rapidly making headway, stimulated by the splendid work of the American Society for Testing Materials[1] and other technical organizations, as well as standards for the testing of those products, such, for example, as the well-known standard of chemically analyzed samples of nonferrous (and other) metals provided by the U. S. Bureau of Standards. The industry refuses to work longer in the old darkness; the light is being let in.

Finally, still another indication of the new research spirit in the industry is the increasing willingness and even desire on the part of individual companies to exchange information with others and even to undertake coöperative research work such as that of the Copper and Brass Research Association and of the American Society for Testing Materials.

Granted now the remarkable mental growth within the industry and its new activity in research, what are some of its features?

The Corrosion Problem

With the exception of electrical copper, the light metals and alloys, and those used for bearings and solders, metals and alloys other than those with an iron base are used in the arts to-day, as always, because of their greater resistance to corrosion. If there is any positive term with which we might properly name the nonferrous metals, it would be "corrosion-resistant" metals. As this is their *raison d'etre*, commercially speaking, it is naturally the chief concern of most of the producers and users of nonferrous metals.

The demands made upon metals in regard to their resistance to corrosion are more and more severe, particularly those of our expanding chemical and allied industries, which are demanding alloys for pipes, vessels, autoclaves, valves, etc., to withstand the action of the many chemicals with which they deal, and under severe conditions of temperature, pressure, velocity of flow, etc. The development of these industries depends in a large measure on the success with which these demands are met, and with this in view the American Chemical Society at its recent New Haven meeting held a symposium on the subject of materials for the construction of chemical equipment.

Users of metals are evincing a more critical attitude toward their use; they are more willing to consider the installation, in place of iron and steel, of the more expensive, but more durable nonferrous metals, such as for roofs and plumbing, because of the rising labor costs of repairs and renewals. The Copper and Brass Research Association is doing much valuable educational work in demonstrating the economies which may result from the adoption of nonferrous materials. Consumers are, however, in many cases reverting to the cheaper steel and protecting it by various coatings.

[1] The nonferrous industries working within this society have provided about forty standard specifications for its products.

Perhaps the noise of the exertions of the steel industry in producing "stainless" and "resist-all" steels has created an alarm within the industry and a fear that unless something is done, their cheaper cousin, steel, will supplant the nonferrous base metals for spoons and pots and plumbing as it once did centuries ago for axes and hatchets. Certainly competition, both within and without the industry, is having a good deal to do with the recent accession of interest in this subject. Consumers ask more questions and have more exacting requirements to-day than ever before. They wish to cease guessing; they want to know.

Along these lines each nonferrous group is active, but a much more striking evidence of the value the industry attributes to this problem is the existence of a number of coöperative research groups devoting their time to it. The British Institute of Metals has for a number of years maintained an active Corrosion Research Committee, which has presented six very useful reports. More recently in this country a similar committee has been organized under the auspices of the National Research Council, and will devote its energies primarily to the elucidation of the fundamental factors and the mechanism of corrosion. At the same time a committee (B-3) of the American Society for Testing Materials, and committees of the American Institute of Chemical Engineers and of the American Foundrymen's Association, have been formed to give consideration to the proper methods for corrosion-resistance testing of nonferrous metals.

It seems safe to predict that our knowledge of corrosion and our practice of studying it will in the course of five or ten years be greatly advanced, and it may be possible at some future time for engineers to predict the course and extent of corrosion with the accuracy and confidence comparable with that with which they design structures to resist mechanical stresses.

Mention might be made of the very illuminating scrutiny to which the various theories of corrosion are being subjected, particularly the electrolytic one and what may be called the chemical or oxygen theory. There are two rather positive schools of thought on this subject just now and the clarifying results of their strenuous discussions can readily be foreseen.

What Is to Be Done with Scrap

The problem of the disposition of its alloys and scrap is an intimate one with every user and producer of metals, and each manufacturer is meeting it as best he can—there being little evidence as yet of concerted action toward general solution of the problem. Naturally, it grows worse each year instead of better, since a portion of each ton of new metal sold comes ultimately on the market as scrap and must be taken care of. No statistics are available, except during the war and post-war periods in which conditions were unsettled, but the ratio of new metal to old used in producing nonferrous mill ingots and sand castings is steadily decreasing, just as the ratio of pig iron to steel produced is decreasing year by year. The complete solution of this problem will lie in many directions. Two of its prominent aspects which will well illustrate its nature are—the steady accumulation of impurities on repeated re-melting and re-working, and the difficulty of positively identifying without chemically analyzing each piece of scrap.

Considering the first item in the light of a well-known thermodynamic principle, the summation of the operations of industry in buying and selling would ultimately result in the degradation of all metals into one form of alloy containing everything (!), were it not for the scrap dealers, the "Maxwell demons" in the industry who exert themselves to keep certain alloys well separated throughout their course and returned to the producer for re-melting, practically intact, and the secondary metal refiners who separate other scrap alloys into their constituents and thus tend to maintain the "entropy" of the industrial alloy system within bounds.

The refining of scrap into secondary metal of value is probably still in its infancy. It requires a different technic than that of the separation of metals from ores, and although there are now being carried out a number of operations of this sort, the volume of this secondary metal business must constantly increase and its character change and increase in complexity and refinement.

At present only the principal metal values are often obtained, such as in the recovery of pig copper from brass, with considerable loss of minor but valuable metals. Or small amounts of the secondary elements are left which depreciate in value of the base metal, such as is generally the case in the brass foundry, secondary metal industry—for example, secondary yellow brass ingot may contain small amounts of aluminium.

This indicates another line of partial solution of the secondary metal problem, and one to which active effort is being given just now in many plants—that is, the acquisition of more exact knowledge of the maximum amounts of impurities which may practically be harmless in different alloys and metals. Although in many cases the evil reputation which certain impurities enjoy—such, for example, as aluminium in red brass, antimony in copper, tin in aluminium—is well justified and often structurally understood, in many others it rests partly on tradition. For example, in the early days of aluminium bronze it was considered absolutely necessary to keep iron out of the metal; subsequently, it was shown that iron in even greater amounts actually benefited it and is used generally for that purpose to-day.

Considerable research is being carried out by individual companies as well as by coöperative groups in an effort to establish more accurate and fundamental understanding of the effects of usual impurities in metals and alloys, with the idea both of real protection to the users of such materials in the case of actually harmful impurities and of eliminating unnecessary restrictions of chemical composition in specifications for elements which are demonstrated to have little or no harmful effects within wider limits than are now accepted. Although many are thinking and working along these lines, the work of the Naval Gun Factory of the Washington Navy Yard on manganese bronze deserves special mention.

The scrap metal itself, particularly around foundries, before remelting into secondary ingot metal could be handled much more efficiently were there quick methods available for identifying the individual pieces. Thus, if the amount of iron or of aluminium in brass scrap could be determined in a few seconds, pieces having excess amounts could be separated and the quality of the secondary metal produced greatly enhanced. A start has been made along this line in studies of the availability of the magnetic method (for iron) and the spectroscopic method for the identification of small amounts of different impurities. The Bureau of Standards and the American Brass Company have done some pioneer work in this direction.

It is interesting to consider what will be the aspects of the metallurgical industries when the source of all metals and alloys is the scrap pile. Certainly, a new metallurgy of metal refining must be born.

Chemistry of Metals at High Temperature

Unfortunately, practically all we know about the chemistry of metals is valid only within narrow and low temperature ranges; what happens at temperatures at which metals are melted and cast, at temperatures at which they are hot-worked, and at temperatures to which they are often subjected in service, is known only in barest outline. All metals normally contain small amounts of oxides, sulfides, and gases—particularly hydrogen, carbon monoxide, sulfur dioxide—as well as in many cases, arsenides, nitrides, carbides, etc., in addition to their metallic impurities. The former are either present in the original metals or, oftener, absorbed from the refractories or slags in the melting furnace or from the fuel gases or furnace atmosphere.

All these impurities may exercise a profound effect on the course of manufacture of the metals and on their properties in the finished form, and many are known to do so, but unfortunately that knowledge is very meager. It can generally be expressed in some such manner as this: "The bronze was brittle because it was oxidized," or "Aluminium is very sensitive to the absorption of gases during melting."

Many individuals are beginning to realize the necessity of obtaining precise knowledge along these lines of it and are trying to attack the problem as best they can. More has been said and done on the gas absorption problem than on any of the other features of this subject, since the production of sound and dense castings and ingots is almost a *sine qua non* of the manufacturing nonferrous industry. The whole subject is, however, a difficult one and will require the development of a new investigative technic, but it is nevertheless extremely important. Exact knowledge of the chemical relations between the metals and the impurities to which they are subjected during manufacturing and refining must be the basis for economical operation of mill and foundry; rejections of off-heats and defective castings will be eliminated when these matters are better understood. Furthermore, such knowledge must be the basis for the broad development of the secondary metal industry which was forecast above. Pure metals may be dealt with in some ignorance, but impure ones require knowledge and care both in their preparation and in their use. Complete knowledge of slag and gas reactions with metals at high temperatures will permit of their refinement and separation from undesirable impurities.

NEW INDUSTRIAL USES FOR NONFERROUS METALS AND ALLOYS

The business depressions following the war have stimulated development work in each group to an unusual degree looking toward the increased commercial application of its products, and many concerns have actually organized products-development departments with engineering and scientific personnel. The copper producers have gone still farther and have initiated coöperative development work through the instrumentality of the Copper and Brass Research Association.

Most of this work is intimately connected with, and indeed based upon, research work, of which the results are continually yielding information as to new products with valuable properties and new applications of newly discovered valuable properties of old materials. Much of this material is in direct response to the more and more diversified and severe requirements of the metal users, each requiring a material for a special purpose and to meet new and exacting conditions. It is going on in all the nonferrous groups, but perhaps it is most active in the aluminium, magnesium, nickel, and zinc groups; the producers of some of the rare metals have also been active—for example, metallic tantalum has recently been the subject of development.

This development and research activity represents a common purpose but hardly a trend, unless we realize with satisfaction the general value to all industries of the mass of practical and useful information which is daily being secured in the effort.

FABRICATION OF METALS AND ALLOYS

Few, perhaps, realize the study and effort necessary to produce a new product and to fit it for industrial utilization. It is not enough to discover and market a new alloy of useful properties; if it is to enjoy any general use, methods must be developed by which it may be fabricated into the various forms desired. This often requires more time and effort than the discovery of the product itself—and, conversely, a new product is valuable somewhat in proportion as the methods of its fabrication are generally known and understood.

The details of various developments along these lines—machining, welding, forging, drawing, spinning, casting, etc.—would be of little interest here. Two developments of this sort, however, seem to be increasing in favor and usefulness. One is the development of the centrifugal casting of metals, particularly of tube and ring forms, which seems to offer much promise both in economy of cost and increase of quality. The other is not very new—the increased use of chill molds in the production of castings which have to be duplicated a large number of times, and in particular the increased use of pressure die castings.

Chill castings are now being produced in brass and bronze and pressure die castings of intricate form in lead, tin, zinc, and aluminium base alloys. Only the lack of a satisfactory mold material prevents the possibility of producing pressure die castings in brass and bronze which could thus be cast to size and require little or no machining.

CONCLUSIONS

Out of the mass of research work now in progress in the nonferrous industries have been selected those features which appear to be the most fundamental and to have the greatest permanent significance for the industry. Extremely valuable and interesting work along more special lines, such as fundamental studies of the structure of metals and alloys by microscope and X-ray, the production of corrosion-resistant coatings by new and old methods, the study and diagnosis of the many curious so-called "diseases" to which some alloys are subject, the development of the use of the electric furnace in both the rolling mill and the brass foundry, the coöperative research initiated by the Engineering Division of the National Research Council, and the American Foundrymen's Association on the use and reclamation of foundry sands, have necessarily been neglected.

What has been said will at least illustrate the direction of research in the nonferrous industries, as far as its objects and purposes are concerned. As to its method, which is of vastly greater ultimate importance, enough has been said to demonstrate that within these industries, as elsewhere, not only is increasing effort being put on the solution of the daily engineering problems, but the volume of fundamental research is growing also; research activity is growing, not only in volume, but in depth and self-consciousness.

New Motor Fuel

The Australian commonwealth government is manifesting great interest in experiments with eucalyptus oil as a motor fuel. C. M. Dyer is said to have demonstrated that it can be used in petrol engines, with efficient means of vaporization. The only difficulty he has encountered is that it will not start an engine from cold without priming, but its calorific value is high. Tests made with cheap cars showed 24 miles to the gallon with gasoline; 28 miles with half gasoline and half eucalyptus oil; and 36 miles on eucalyptus oil alone. Eucalyptus oil mixes with gasoline, benzene, and alcohol, and acts as a decarbonizing agent. The main difficulty of manufacture on an extensive scale would be in securing laborers to gather the leaves.

The Application of Research to Plant Problems in the Ceramic Industry

By Percy C. Kingsbury

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THERE is nothing spectacular about the manufacture of clay products, no vast fortunes have been made in the ceramic industry, and there are few aspects that attract more than the casual interest of the "man in the street." It is therefore not surprising that the importance of this industry is seldom realized even by those who are engaged in it, and a short survey may be permitted.

Percy C Kingsbury

Strictly speaking, the ceramic industry comprises only the manufacture of ware from burned clay, which may be classified according to its applications as follows:

Building Purposes. Building brick, paving brick, hollow tile, sewer pipe, roofing tile, terra cotta, sanitary ware, floor tile, wall tile, drain tile.

Industrial Purposes. Fire brick, fireclay shapes, chemical stoneware, chemical porcelain, electrical porcelain, spark plugs, conduits.

Domestic and Art Purposes. Stoneware, china, porcelain, faïence.

This classification covers only clay products, but the ceramic industry is now usually considered to cover the manufacture of special brick made of silica, magnesite, carborundum, etc.; abrasives like emery or carborundum in the form of wheels, blocks or grain; glass, cement, and lime products; fused silica ware and enamels for iron and steel.

From this broader point of view the manufacture of ceramic products is one of the most important industries in this country, with a production exceeding in value one billion dollars per year.

In common with most American industries, the ceramic industry is handicapped by lack of research work on the various problems that the manufacturer has to meet, and the object of this paper is to indicate the institutions that are carrying on research in this field and to suggest how these facilities can be utilized to the best advantage to the industry.

Institutions Doing Research in Ceramics

At the present time there are two government institutions operating ceramic research departments—the Bureau of Standards at Washington, D. C.; and the Bureau of Mines at Columbus, Ohio, and New Brunswick, N. J.

There are five state educational institutions offering a course in ceramics. These are: Rutgers College at New Brunswick, N. J.; Alfred University at Alfred, N. Y.; Ohio State University at Columbus, Ohio; the University of Illinois at Urbana, Ill.; Ames University at Ames, Iowa; and another is proposed for the Georgia School of Technology, Atlanta, Ga.

Fellowships at the Mellon Institute of Industrial Research have been endowed for the study of enamel, refractories, and vitrified tile, and several of the large corporations in the ceramic industry have their own research departments. The work of the latter is, however, not generally available to the industry, except in so far as their work is made public through publication in technical journals.

A few special branches of this industry operate their own research departments, of which the National Lime Association is an example. In addition to these facilities every institution doing general research work is naturally engaged in ceramic problems from time to time.

No better object lesson of the value of research to the ceramic industry could be found than an examination of the wonderful results achieved by the research departments of these institutions during the war.

The demand of the United States Government for American-made materials for the prosecution of the war was imperative and in some cases almost frantic, and we then perhaps for the first time came to a realization of the extent of our reliance upon Europe, and more particularly Germany, for our ceramic products.

Spark plugs of superior quality, lenses for telescopes, field glasses and scientific instruments, chemical glassware and porcelain are a few important products for which we were for all practical purposes dependent upon Germany. The efforts of our ceramic research departments in meeting these demands were so successful that in some instances, of which chemical glassware is perhaps the most conspicuous example, the domestic product is now superior to the imported, and many new and important industries have thus been permanently established in this country.

Although the results achieved with our present facilities for ceramic research have been remarkable, they are very far from adequate to the needs of this industry. Let us therefore see how these facilities are now being utilized and what can be done to develop them.

Kinds of Research

Research as applied to the ceramic industry may be roughly classified thus:

(1) Investigation of characteristics of raw materials and finished products.

(2) Purely academic research.

(3) Research applied to specific problems in the plant either to improve the product or reduce cost of manufacture, and investigation of the application of the product to the requirements of the market.

(1) The physical constants of raw materials and finished products are slowly being evaluated. These are the foundation of all research and without them no useful work can be carried out. These data, compiled by the National Research Council, if not yet entirely adequate to the

needs of the industry, are a most valuable contribution to them.

This is properly a function of the government institutions devoted to industrial research as the benefits derived accrue to the entire industry and the work has a direct bearing on the utilization of national resources.

(2) A considerable amount of the research work that is carried out is purely academic in character. This is and can perhaps best be carried out by the large universities, by private individuals, and by the research departments of large corporations which have the necessary resources and personnel and the vision to realize that this class of work is not only the most interesting, but also the most profitable in the long run.

As a rule these two classes of work have no immediate bearing on problems in the plant. We are therefore only indirectly concerned with them at this time, but it should be borne in mind that they are of the most vital importance to the industry.

(3) Problems arising in the plant and in the marketing of the product can in almost all cases best be attacked by methodical experiment. Unfortunately, however, it is still the rule rather than the exception for such problems to be approached by trying haphazard "hunches" in the hope of making a lucky guess. The money wasted in these invariably futile efforts is in most cases much more than would be required to conduct an investigation that would not only solve the specific problem under consideration, but would also establish principles for the solution of all problems of a similar nature.

The research facilities available for handling such problems are inadequate, but what is of still more importance, the present facilities are neither fully utilized nor appreciated by the industry. One reason for this is that we are trying to "sell" to the wrong people the advantages of research to the ceramic industry. The technical man to whom such appeals are ordinarily addressed is already convinced. It is to the nontechnical executive that these advantages must be presented. Many of these executives think they have taken full advantage of all that scientific investigation has to offer towards the solution of their problems when they have hired a chemistry graduate for $30 per week who is expected to find an immediate explanation for all the various difficulties that arise in the plant. When these results are not forthcoming they are more than ever convinced of the futility of attacking plant problems in this way.

This type of executive is passing, but he still controls a majority of the smaller plants in the country, and an entirely new attitude of mind on his part towards research as applied to plant problems must therefore be cultivated.

This can best be done by using an avenue of approach with which he is familiar. Research service should be offered him as a frankly commercial proposition and sold just as advertising service, investment service, or insurance is sold—that is, by personal solicitation and popular advertising.

We have in the Mellon Institute of Industrial Research an excellent model of the type of institution required for furnishing this service. The work of the Mellon Institute is, however, intended in general for interpretation by technical men, whereas the institution we are considering would have the more difficult problem of presenting the results of its investigations so as to be intelligible to those who may be presumed to have a thorough practical knowledge of the industry, but otherwise no special scientific training.

It is perhaps hardly proper to dignify as "research" much of the work that this institution would be called upon to do. It is reasonable to expect that most of the problems that would be presented to it could be solved promptly by a reference to technical literature or by the application of known physical or chemical principles. Such experimental work as might be required would seldom tax the resources of a well-equipped physical and chemical laboratory.

The cost of operating such an institution need not therefore be excessive—in fact, the cost of selling this service is likely to be the more important item of expense.

In order for the service to be effective it will frequently be necessary for the institution to have access to the plant and operating data of the client, who would therefore have to be convinced of the ethical standards of those entrusted with the work. This could best be done by placing the institution under the control of the universities or technical schools in much the same way as the Mellon Institute is associated with the University of Pittsburgh.

There is an adequate supply of young technical men capable of handling under proper supervision such problems as might be presented to this institution, and another type of man could be trained without much difficulty to present this service to the industry in a tactful and dignified way.

The success of the enterprise would, however, depend almost entirely on the personality of the director. He would have to be a man of broad scientific attainments and at the same time of much experience in the industrial field, capable of seeing a problem from the viewpoint of the worker in the plant and of discussing it from the same viewpoint.

At the present time if the executive of the small plant that is without a technical staff is interested to know how scientific research can help in the solution of his plant problems, he has to hunt for the information himself, and if he is not interested no special effort is made to attract his attention in this direction. By the establishment of the facilities we have been considering the advantages of closer coöperation with the technical man would be placed directly before him in a way that would compel his serious consideration and the technical man and he would be brought into personal contact on a plane of mutual interest.

This will go a long way towards breaking down, on one hand, the supercilious attitude of the young technical man towards the business man who does not think as he does, and, on the other hand, the impatient intolerance of the nontechnical executive with the assumed lack of business acumen of the former.

The foregoing observations have been made with particular reference to the ceramic industry because that industry would perhaps benefit more than any other by a closer coöperation between the technical man and the executive in the plant. Most of these remarks are, however, obviously applicable to other industries, and there is no good reason why an institution as outlined should confine its activities in one particular groove.

New Oil Cracking Plant

At the present time a number of processes for the manufacture of motor spirit from heavier oils are being discussed. These hail chiefly from Germany, and some remarkable results are reported. It is understood that one of these processes will be exploited in a new plant to be erected at Chester, by the Anglo-Scottish Finance Corporation, Ltd. The process to be adopted there is the discovery of a German chemist, Dr. Wolf, who has stated that there is no specific influence of hydrogen in the Bergius process.

The new process is reported to be something quite different from the ordinary cracking methods, and is described as a splitting process which takes place under much less drastic conditions than those usually employed. Yields of up to 70 per cent are claimed, and it is understood that the process was most thoroughly investigated in a semilarge-scale installation before the scheme of manufacture was embarked upon in this country.

Chemistry in the Cereal Industries

By C. H. Bailey

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CEREAL chemistry has not only attracted a constantly increasing number of devotees during the past decade or two, but has constituted a profitable research field. The milling industry, like many other industries, has recently found the chemical laboratory a worthwhile adjunct to the plant. Cereal breeders have utilized the services of chemists and flour-testers in developing and propagating new wheat and other cereal varieties. More recently, bread, cracker, macaroni, and cereal food manufacturers have employed chemical methods in developing their processes and in connection with purchase of raw materials.

Keen interest in the problems of these various branches of the industry has naturally inspired the research chemist to work in this field. Thus, the principal interest of the chemical departments of several state agricultural experiment stations has, at times during this period, been attracted to cereal problems. Various bureaus of the U. S. Department of Agriculture have likewise contributed in large measure to the acquisition of useful knowledge. An extensive literature of the subject accordingly exists in the files of government and state experiment station bulletins. Added to this is the rather widely scattered literature in the form of journal articles, contributed from the laboratories mentioned, as well as by numerous chemists associated with universities and various private institutions. Lack of space prevents an enumeration of the foreign institutions which have likewise published on various aspects of cereal problems. They are to be found in practically every civilized country of the world. A complete bibliography of the literature in the last twenty years, even when restricted to purely chemical considerations, proves to be an extensive affair indeed.

C. H. Bailey

It is, however, worth while to mention certain specific subdivisions of the general subject which the activities of the chemist have touched. These include the biochemistry of the phylogeny and classification of wheats; wheat breeding for strength and disease resistance; progressive development of the plant and the kernel; biochemistry of certain cereal diseases; effect of premature freezing and of sprouting on the chemical and other properties of the crop; grain storage, particularly with respect to respiration; grain standardization and grading; wheat conditioning and tempering; chemistry of milling; flour bleaching; flour improvers, including a large group of various organic and inorganic substances; enzyme phenomena, including particularly those occasioned by zymase, diastase, and the proteases; chemical changes involved in various processes of baking; control of bread diseases, particularly rope; staling of bread; bread wrapping; in addition to extensive consideration of cereals and cereal products in the nutrition of man and animals.

Certainly, this affords a wonderful field for work, both research and control. Such a variety of problems is presented that the facilities of every branch of modern chemistry can be utilized in their solution. Constituting, as it does, a subdivision of applied biochemistry, it can, like biochemistry generally, make use of the methods of inorganic, organic, and physical chemistry. It is interesting to trace the development of methods employed in such work, as illustrating the processes of thought. A brief quarter century ago interest was centered largely in the study of wheat proteins. The work of Fleurent had suggested that variations in flour quality, and particularly in baking strength, exhibited by flours of the same total protein content might be attributed to differences in the ratio of gliadin to glutenin. This pronouncement stimulated a vast amount of investigational work, and even in control laboratories thousands of gliadin determinations were made. Osborne's notable researches on the wheat proteins added substantially to our knowledge of their chemical constitution. Enzymes soon received their share of attention, and diastase activity was found to be correlated with baking strength. About this time the colloid chemists emerged as a distinct group, and colloidal properties of flour, and particularly of gluten, began to receive their share of attention. The most notable pioneer work in this field was doubtless that of Wood and Hardy, who maintained that in the absence of electrolytes gluten possessed neither tenacity nor elasticity. The concentration and character of salts present were believed by them to determine the physical properties of gluten. Jessen-Hansen then called attention to the significance of hydrogen-ion concentration in the production of bread, a theme which has been much elaborated upon during the past few years. Thus, we observe that the physical chemist has definitely appeared as a factor in the development of flour research. And still more recently, in point of chronological sequence, it has been made evident that, while the proportion of the several amino-acid groups present in the gliadin and glutenin of strong and weak flours may not vary appreciably, there is a possibility that the relative size of their molecules or aggregates may be far from constant. Recent studies of Gortner and his co-workers lead to the conclusion that the glutenin of typical strong glutens exists in larger aggregates than does glutenin of weak gluten. These differences are indicated by the hydration capacity of glutenin in contact with dilute acids.

It is quite evident that, while cereal chemistry has utilized the services of the physical chemist on the one hand, it has enjoyed close relations with the biologists on the other hand. Mention has been made of the coöperation effected between agronomists, plant breeders, and the chemists. More recently, the biochemist has actively engaged in a study of the fungi, and there is need of further work along this line. The production of ordinary yeast-leavened bread involves the activity of several organisms. Gases of fermentation are produced through the metabolism of yeast. This fungus responds readily to modifications in its environment. Temperature, hydrogen-ion concentration, and the character and concentration of the sugars and salts in the dough solution are important in controlling the activity of yeast. Considerable progress is being made in the direction of supplementing the deficiencies of a simple dough by the deliberate addition of salt and acid-reacting mixtures which "improve" the mixture by accelerating yeast activity.

Not only yeast, but other organisms are concerned in fermentation and baking. Thus, the dough batch is far from sterile, and doubtless contains bacteria-producing lactic acid and other organic substances. It has been suggested that active, pure cultures of certain lactic acid bacteria, or sour mashes produced through their activity, be added to bread doughs to increase their hydrogen-ion concentration. Such practice, if common, would necessitate a careful physiological and biochemical study of the organisms employed, with a view toward the development of satisfactory control methods.

Certain bread diseases, notably rope, which is caused by a spore-forming organism of the potato bacillus group, occasion considerable losses. The physical chemist, in the person of Dr. Henderson, has indicated convenient and adequate methods of preventing the depredations of these forms by controlling the hydrogen-ion concentration of bread, particularly during hot seasons of the year. Further efforts are necessary in the direction of controlling bread molds, which occasion considerable losses under certain conditions.

One of the attractive possibilities now unfolding before the bakery chemist is the production of "instantaneous bread." This term is coined by the writer to describe bread made without fermenting the dough for any considerable period. At least two types of doughs have recently been suggested as lending themselves to this unique procedure. The first involves an acidulation of the dough, which thus has approximately the same hydrogen-ion concentration when freshly mixed that an ordinary dough acquires after four or five hours of fermentation. In the second process, the dough is brought to a temperature about 5° C. above the normal (27° C.), and a somewhat increased charge of yeast may be used. Whichever procedure is followed, the reduced fermentation period effects economies in several ways. Less floor space will be required in the dough room, the labor cost should be somewhat less, and, what is even more significant to the chemist, losses in fermentation will be reduced and the yield of bread correspondingly increased.

It now remains for some ingenious chemical engineer to render the bread-baking process continuous and automatic. As yet it is only partially automatic. Dividers, molders, proofers, and traveling ovens have been assembled in one complete, synchronized, automatic unit. We now need to start at the head of the process, and assemble automatic mixing machinery which will continuously deliver a homogeneous dough with proper and uniform composition, hydrogen-ion concentration, and temperature to the dough-divider, which is already coupled to the necessary appliances for completing the process.

Not only has the chemist invaded the milling and baking industries, but he is making his impress on the cracker and biscuit industry. Several biscuit and cracker plants have chemists and chemical laboratories. Active research in this field is also in progress in several private institutions, as well as in at least two universities. Part of the university research is maintained through the medium of industrial fellowships financed by far-sighted individuals connected with this industry.

No mention has been made of the large volume of wheat now being merchandised on the basis of chemical composition. Considerable proportions of the Kansas hard winter wheat crops the past few seasons have been sold with a guaranteed crude protein or crude gluten content. This practice has been extensively adopted in merchandising the northwestern spring wheat crop of 1922. The time may not be far distant when wheat standards will include crude protein specifications, particularly so far as the requirements of the several sub-classes of hard wheat are concerned.

Thus, we note that chemical methods have become extensively used in all branches of the cereal industries. This is being reflected in the type of training demanded by specialists in other fields. Geneticists, physiologists, pathologists, agronomists, milling engineers, and bakers are giving biochemistry a more prominent position in the study programs of their advanced students. This is making for a healthy and normal growth of these lines of specialization, and permitting chemistry to render an adequate service.

A Device for Water Analysis and Slow Filtration[1]

By Andrew C. Simmons

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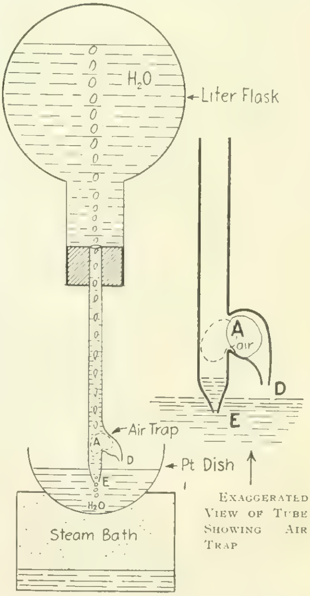
THE accompanying sketch shows a simple device which has been found satisfactory for water analysis and for slow filtration at the University of Florida. To get total solids by means of steam evaporation the apparatus is set up as shown and the water from the flask is fed into the platinum dish as fast as the water in the dish is evaporated off. This device is useful also in filtering colloidal solutions.



Exaggerated View of Tube Showing Air Trap

A is a fairly large air trap in which air is imprisoned after entering through the opening *D*, which is open to the air at all times. The air entrapped exerts a slight pressure downward onto the water, which rises slightly at *E*. So long as the end *E* extends into the water far enough so that water pressure exerted above *E* equalizes the pressure exerted by the entrapped air, there will be no flow of water from the flask into the dish, but when some of the water in the dish has evaporated so that the entrapped air pressure is greater than the water pressure upward on *E*, then the bubble of air in *A* is drawn downward slightly towards *E*, and at the same time more air is drawn through *D*. Bubbles of air then enter through *D* and rise up through the tubing to the top of the flask. This causes an increased air pressure on the head of water in the flask and water drops down through the tube and enters the dish, beneath *E*. This flow continues until once more the water pressure upward on *E* equalizes the entrapped air pressure. This starting and stopping of the flow of water continues until all the flask has been emptied.

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[1] Received May 18, 1923.

The Potentialities of Catalytic Research in the Chemical Industry

By Hugh S. Taylor

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THE potentialities of catalytic research constitute a problem which must continuously confront the executive officer of any large chemical organization. How prepared for developments along catalytic lines should such an organization be? Is it worth while to carry on the payroll a specialist in such a particular branch of the subject? The answers to such questions are most important in any well-ordered concern. A resumé of some problems and a brief record of some progress may help towards such answers.

Hugh S. Taylor

Lower Operating Temperature of Catalysts

Sabatier, in his text on "Catalysis in Organic Chemistry," states that ethylene and hydrogen begin to combine rapidly in presence of active copper above 150° C. A recent article by Pease[1] calls attention to the fact that by reducing copper oxide under controlled conditions a copper of such activity may be obtained that immeasurably rapid reaction of the same two gases is obtainable at 0° C., *with the vessel containing the copper in an ice bath.* The hydrogenation of ethylene is not likely to be of commercial interest in the near future, but one cannot be blind to the potentialities which would result from a reduction of 150 degrees in the operating temperature of all catalytic agents. For example, in ammonia synthesis, operation at 350° C. instead of the usual 500° to 600° C. would enormously increase the possible yield per gas passage as a result of the more favorable equilibrium conditions; or, what would amount to the same thing in the end, the lower working temperature would make possible the use of lower working pressures than are now required for a given yield at the higher temperatures. Simplification of operation and less risk and danger might thereby be achieved. That such an eventuality is realizable seems to be indicated by the results recently communicated at the spring meeting of the AMERICAN CHEMICAL SOCIETY on the ammonia equilibrium at 30 atmospheres pressure. It is hard to believe that such studies were made unless operation at 30 atmospheres pressure were within the realm of practical achievement.

Control of "Poisoning"

Everyone interested in the problem of catalysis is familiar with the "poisoning" of catalytic agents. This factor of poisoning still constitutes one of the bugbears of the industrialist and it is the subject of anxious queries put to anyone desiring to initiate new catalytic processes. It is refreshing, therefore, to be able to record that "poisoning" is now being brought so under control by the scientific investigator as to be susceptible of use for desired ends. The recent researches of Rosenmund, Zetsche, and Heise[2] have demonstrated that reactions which may not go when the utmost purity of reagents is secured, may be carried out by the addition of suitable impurities to the reaction system. Palladium, for example, may be partially poisoned by a variety of substances in such a manner that the chief reaction product of the reduction of benzoyl chloride may be one or other of the substances benzaldehyde, benzyl alcohol, benzyl benzoate, dibenzyl ether, or toluene, the product obtained being determined by the nature and amount of the added substance. As typical of such substances, quinoline, quinoline heated with sulfur, xanthone, and dimethylaniline may be cited. This constitutes a new method of preparation of aldehydes hitherto unprepared. Zetsche has extended the work to dehydrogenation of alcohols with accompanying oxidation. In this case aldehydes, acids, and esters may result. Aldehyde is the preferred product if to a copper catalyst small amounts of quinoline are added. Nitro bodies further assist. Added to nickel, however, quinoline promotes acid and ester formation. It is not possible to give the details of this fascinating work, which is now quite extensive. Its implications, however, cannot be overlooked by either the theoretical or the practical student.

Controlled oxidation is of the greatest importance in technology. Especially in the field of hydrocarbon oxidation would the application of Rosenmund and Zetsche's principles lead to most fruitful industrial results. Oxidation of methane, ethylene, and other simple hydrocarbons to yield formaldehyde is always accompanied by a variety of other undesired oxidation products. A catalyst, modified to produce formaldehyde alone, would be a most useful discovery. The same holds true also of such oxidations as those of naphthalene to phthalic anhydride, of anthracene to anthraquinone, and of benzene to maleic acid. In all these cases the danger of producing undesired oxidation products necessitates a most rigid, narrow, and inflexible set of experimental conditions. How far it is possible to obviate such limitations by controlled catalyst poisoning is worthy of study.

Our knowledge of the underlying causes of catalyst poisoning is growing steadily. Maxted's[3] researches have demonstrated that poisons for platinum and palladium hydrogenation catalysts cut down the adsorption of hydrogen by the catalyst. Pease[1] has shown the same to be true as regards the adsorption of hydrogen, ethylene, and carbon monoxide (private communication) for a copper catalyst poisoned with mercury. Taylor and Burns and Gauger[4] have shown that diminished adsorption by a nickel catalyst may be secured by controlled heat treatment of the metal.

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[1] *J. Am. Chem. Soc.*, **45**, 1196 (1923).

[2] *Ber.*, **54**, 425, 638, 1092, 2033, 2038 (1921).

[3] *J. Chem. Soc. (London)*, **115**, 1050 (1919); **117**, 1280, 1501 (1920); **119**, 225, 1280 (1921).

[4] *J. Am. Chem. Soc.*, **43**, 1277 (1921); **45**, 920 (1923).

This is verified also in the work of Pease and in that of Benton[5] for oxide catalysts. The effect of the heat treatment parallels roughly the effect of controlled poisoning. That such manipulation of a catalyst may lead to useful results is to be expected, since by such means the relative concentrations of reacting materials can be in part controlled. Benton's researches have shown that the preferential catalytic oxidation of carbon monoxide in presence of hydrogen, at oxide catalyst surfaces, is to be associated with the relative adsorptions of the two gases by the catalyst. When such concentrations of adsorbed materials can be manipulated at will, the province of preferential reactions will be enormously extended.

THEORY OF INHIBITION OR NEGATIVE CATALYSIS

It is twenty-five years since Bigelow studied the peculiar property exercised by a variety of organic compounds such as benzyl alcohol, benzaldehyde, glycerol, mannite, and phenol in arresting the oxidation of sodium sulfite solutions. Young[6] extended Bigelow's study showing that such substances as nicotine and other alkaloids, ammonium salts, and potassium cyanide behaved similarly towards sodium sulfite solutions. He also showed that the oxidation of stannous chloride solutions could be similarly inhibited. Lumière and Seyewetz[7] also showed that the inhibitory substances of sulfite solutions included hydroquinone, pyrocatechin, pyrogallol, paraminophenol, paraphenylenediamine, glycine, etc. This is of importance in view of more recent results. Somewhat earlier than this Titoff,[8] attempting to elucidate the mechanism of the action of such inhibitors, demonstrated that the oxidation of sulfite solutions was accelerated markedly by the most minute traces of positive catalysts, notably copper salts. A solution of copper sulfate as dilute as 0.1^{13} molar was shown to produce perceptible acceleration of the rate of oxidation of the sodium sulfite solution. Parenthetically, it may be observed that it was this activity of copper which was utilized recently by Mack, Osterhof, and Kramer[9] in their determinations of the vapor pressure of copper and copper oxide at relatively low temperatures. This study of Titoff, demonstrating the enormously sensitive nature of sulfite solutions to positive catalysts, led him to suggest that negative catalysts act by suppression of minute traces of powerful positive catalysts. In this way the small amounts of negative catalyst sometimes adequate to inhibit a reaction almost completely found a ready explanation. In considering such a situation it might suggest itself to the critic to inquire why it is more difficult to comprehend negative catalysis by substances in minute concentrations than it is to accept positive catalysis in such marked dilutions as those discussed above; why, for example, one gram mol of copper in 55 million million mols of water should speed up a reaction if one gram mol of a substance in ten thousand mols of water should lead to doubt and disbelief when acting as a negative catalyst. It is nevertheless true that Titoff's work has colored most of the subsequent work on the subject of negative catalysis; it is still the most quoted "explanation" of negative catalysis. It may be argued, with a considerable degree of confidence in view of recent history, that the general acceptance of Titoff's viewpoint has retarded the development of this fascinating and increasingly important branch of the subject.

A few other cases of inhibitory power are known. The luminescence of phosphorus in air or dilute oxygen gas mixtures is suppressed by sulfurous gases, as observed by Berthollet in 1797 and studied continuously since that time until the present day. It has long been known that a variety of substances inhibit the decomposition, both thermal and photochemical, of hydrogen peroxide. Water, famous as a necessary positive catalyst to a large number of reactions ever since the researches of Mrs. Fulhame in the last decade of the 18th century, is now known as the inhibitor in a variety of reactions in nonaqueous liquid media, notably of the decomposition of oxalic acid in concentrated sulfuric acid solutions.[10] The more observant have frequently noted that benzaldehyde occasionally oxidizes quite readily; at other times it has seemed remarkably resistant to oxidation. Essential oils have shown similar variability. It has been known that the natural essential oils preserve their qualities on keeping better than the chemically pure materials.

Many of these and other observations have been collected by Moureu and Dufraisse[11] in a literature study accompanying their recent important contributions to the problem of inhibition of autoxidation processes. Their earliest work showed that the prevention of autoxidation of a variety of substances—for example, benzaldehyde and acrolein—was possessed by phenolic compounds. The efficiency of such compounds was remarkable. One molecule of hydroquinone suppressed the oxidation of 40,000 molecules of acrolein. Analogous results were obtained with such autoxidizable substances as acetaldehyde, chloral, propionic aldehyde, acrolein, anisic aldehyde, cinnamic aldehyde, hydrocinnamic aldehyde, furfurol, styrolene, turpentine, linseed oil, nut oil, and butter. Furthermore, various secondary phenomena which often accompany autoxidation processes, generally related to molecular condensations and manifested by changes of color, precipitates, change in viscosity, rancidity, etc., are also inhibited by such additions. Thus, furfural, instead of turning deep black, remains almost colorless; acrolein no longer yields dis-acryl, a polymerized product; styrolene remains fluid, no longer giving the soluble resin known as *m*-styrolene; linseed oil can be exposed to the air in thin layers without losing its fluidity (observations lasting three years); butter preserves its organoleptic properties; and, in general, fatty bodies do not become rancid.

Further afield, Moureu and Dufraisse have noted the French patent to the Societa Anonyma Coöperativa (1905) which claims the protection of silks against light, heat, and atmospheric action by means of thiourea, hydroquinone, and their derivatives, this patent being a product of the investigations of Sisley and Seyewetz;[12] also a German patent (1918) to the Badische Anilin und Soda Fabrik claiming the protection of synthetic rubber against autoxidation by the presence of phenolic compounds. In a recent paper communicated by Professor Moureu, Gillet and Giot[13] have noted that materials dyed with azo dyes and eosin dyes are protected against color change by such inhibitors as Moureu and Dufraisse have studied. Rubber oxidation is inhibited by tanning and hydroquinone.[14]

It is very evident, therefore, that there is here a rich field of study, both for the industrialist and the scientist—for the technical man in the applications possible, and for the theoretical chemist in the problems of mechanism which thereby arise. Moureu and Dufraisse, rejecting the Titoff concept of suppression of a positive catalyst, have formulated a theory of mechanism which seeks the theoretical solution of the problem of autoxidation in the "per-oxidation" of both autoxidant and of inhibitor followed by interaction of the two oxidized agents, to regenerate both initial substances and elementary oxygen. Thus, if A be the autoxidizable substance and B be the inhibitor, the sequence of reactions would be

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[5] *J. Am. Chem. Soc.*, **45**, 887, 900 (1923).

[6] *Ibid.*, **23**, 119, 450 (1901); **24**, 297 (1902).

[7] *Bull. soc. chim.*, **31**, 672 (1922).

[8] *Z. phys. Chem.*, **45**, 641 (1903).

[9] *J. Am. Chem. Soc.*, **45**, 617 (1923).

[10] Bredig and Lichty, *Z. Elektrochem.*, **12**, 450 (1906); Lichty, *J. Phys. Chem.*, **11**, 255 (1907).

[11] *Compt. rend.*, **174**, 258 (1922); **175**, 127 (1922); **176**, 624, 797 (1923).

[12] *Bull. soc. chim.*, **31**, 672 (1922).

[13] *Compt. rend.*, **176**, 1402 (1923).

[14] *Ibid.*, **177**, 204 (1923); French Patent 509,667 (1919).

$$A + O_2 = A(O_2); \quad A(O_2) + B = A(O) + B(O); \\ A(O) + B(O) = A + B + O_2$$

or alternatively

$$A + O_2 = A(O_2) \\ B + O_2 = B(O_2) \\ A(O_2) + B(O_2) = A + B + 2O_2$$

Certain data already accumulated lend a degree of credence to this formulation. It is doubtful, however, whether it is applicable in more than a few cases; it would need entirely recasting to cover the general case of negative catalysis, which, as we have seen, includes reactions not autoxidant in nature. An attempt to formulate a more general theory of negative catalysis has recently been made by the writer independently of the work of the French authors.[15] The theory accounts for inhibitory power by assuming interaction between one of the reactants and inhibitor to form a molecular compound, as an alternative to reaction between the two or more reactants. The extent of the inhibition is determined by the degree and velocity of compound formation. The mechanism of Moureu and Dufraisse would be a special case of this more general formulation. The general theory would suggest other possibilities of inhibitory mechanism and thereby a wider range of reactions sensitive to negative catalysis and a more extended series of inhibitory materials.

It should be very evident, therefore, that catalysis, both positive and negative, is a subject that the chemical organization cannot ignore; the theoretical chemist can surely find therein problems that will delight his soul.

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[15] *J. Phys. Chem.*, **27**, 322 (1923).

The Mechanism of Corrosion

By John Johnston

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Harris and Ewing

John Johnston

Of the great number of publications dealing with the general topic of corrosion, few add much to the reader's positive knowledge. Indeed, by their lack of agreement, many of the observations recorded in the literature are likely to confuse and weary him. This appears to arise in part from the desire of an author to show that other products are worse than the one whose merits he is championing and in part from the fact that many investigations have been limited to a specific set of conditions which have not been defined and controlled with sufficient care. The most important cause, however, is an oversimplification of the problem in an attempt to discover a single primary factor to the operation of which all phenomena of corrosion may be ascribed. The protagonists of several such factors, assumed to be primary, bring forward evidence in favor of their particular beliefs and give reasons why any other explanation is unsatisfactory. This does not mean that evidence has been deliberately manufactured or ignored, but rather indicates that the problem is more complex than many have assumed it to be. In other words, a complete description of the processes of corrosion necessitates the consideration of several factors, any one of which may under some circumstances be dominant. That it could not well be otherwise is evident from the wide range of conditions under which the term "corrosion" is applied—in water, in salt or acid solutions, cold and hot, in the atmosphere, dry and moist, clean and dirty, in air or gases at high temperature. And the medium may be stagnant or in rapid relative motion. Furthermore, we may be dealing with a single metal from any part of the electrochemical series, pure or impure, with a metal made up substantially of a single kind of crystal or containing several kinds of crystal, and the metal may be acting as electrode and under electrical or mechanical stress produced by external causes or internal strains. It is clear, therefore, that in discussing this problem it is almost impossible to avoid dogmatic statements, unsupported by convincing evidence, or generalizations too broad to be useful.

Points of similarity in the diverse conditions have led different writers to attribute the effects to various factors. Adequate emphasis has not been given to one of these, namely, that in all cases of corrosion we are dealing with effects at a surface between at least two, and possibly three, phases. Therefore more attention should be directed to what may be expected to happen at such a surface of separation, and the formation and behavior of a film or layer (using these words in a general sense) at a metal surface under various conditions should be studied. It has long been recognized that in a general way the character of the metal surface is of importance. For instance, polishing lessens the rate of corrosion, and protection from corrosion is achieved if the surface layer be impervious to the corroding agent. But little is known definitely as to why there should be such large differences in the protection afforded by such coatings, even when formed under conditions which appear to be nearly identical.

A clue to the cause of these differences in some cases may be given by the following considerations. When a metal oxide or hydroxide is shaken with water in the presence of carbon dioxide until the system is in equilibrium, the stable solid phase will be hydroxide or carbonate (excluding, for the moment, the possibility of a basic carbonate), according to whether the partial pressure of carbon dioxide at equilibrium is below or above a certain limiting value. This limiting value, or transition pressure, characteristic of the particular metal, is determined largely by the relative solubility of its hydroxide and carbonate, so that it depends upon temperature. At present it is not known for any metal except magnesium, for which it is about 0.0005 atmosphere of carbon dioxide, a concentration slightly greater than that in outside air but less than that commonly present in a room. Accordingly, if conditions are such that equilibrium is attained, in a laboratory we might get magnesium hydroxide when all the windows are open but magnesium carbonate with less ventilation. If equilibrium is not attained, we would get a mixture of the two, or even alternate layers of hydroxide and carbonate. Thus, a piece of magnesium immersed in water exposed to the atmosphere might become coated with hydroxide, with carbonate, or with both. Moreover the structure of the film might be different, according to whether the carbonate had been formed from hydroxide or precipitated directly.

It is possible therefore that the different coatings, which may thus be produced through a relatively small variation of conditions, differ largely in the protection which they afford to the metal. This is a case of a possible factor which has been left out of account as being negligible, but it may in some cases be important and responsible for the lack of consistency of results obtained under apparently identical conditions. For the metals in which we are more interested as subject to corrosion this transition pressure of carbon dioxide is not known, but that in some cases it should be not far from the proportion commonly present in the atmosphere is not improbable.

Incidentally, these considerations lead to the question—are so-called basic carbonates definite compounds and not merely mixtures of hydroxide and carbonate which appear to be definite only because they are usually made under substantially identical conditions? To what extent the partial pressure of carbon dioxide is a factor in the process of corrosion can be determined only by careful work to ascertain what may be expected to occur in the systems RO–H_2O–CO_2 (R denoting a metal) and whether films formed within an appropriate range of concentrations of CO_2 differ in protective power.

This leads to the question of the criteria which can be used to characterize films on metallic surfaces. Films differing in protective power may look alike, even under the microscope, as they are composed of extremely fine particles. Chemical reactions are generally not very helpful, for the quantity of material is small and the observations cannot be interpreted unambiguously. It would therefore seem necessary to resort to physical methods, particularly sensitive electrical methods, as a means of estimating the degree of difference of films produced under different conditions. The electrical resistance and capacity of the films are possibilities and preliminary investigation has indicated substantial differences on making such measurements on films made under different conditions upon the surface of a piece of metal. It is possible also that measurements of electromotive force, thermionic emission, photoelectric effect, catalytic activity, or gas absorption would prove useful in some types of corrosion. Along these lines, however, one could not hope to achieve much except by taking the risk that the systematic investigation which would be required would not be worth the time and effort involved. Nevertheless, it looks as if our knowledge of the mechanism of corrosion will be unsatisfactory until we have learned how to characterize our surfaces and films and to distinguish one from another.

A study of the structure of metal surfaces and of the reactions which may occur at those surfaces is of value also as a means towards a better knowledge and control of the processes of electrodeposition which are still far from being well understood, for the surface of the base affects the properties of the electrodeposit, for instance, its adherence and continuity, and hence its protective power. Thus the problems of corrosion and electrodeposition are closely connected and can with advantage be investigated together, as it would seem that in both processes an important factor in the result is the nature and structure of the first film formed, that is, of the phase which is in immediate contact with the metal.

If hydrogen is passed over pure copper oxide, reduction may not start until a temperature higher than that which suffices to maintain the progress of reduction when once it has started has been attained. Moreover, the reduced area spreads out from the point or points at which the copper appeared initially. This reluctance of the process to start, however, may be obviated by the presence in the oxide of a few particles of copper which serve as nuclei about which the reaction proceeds. This suggests that there is much more likelihood of reaction at a place in the surface where we already have the two solid phases concerned in the reaction, or, at least, when there is some discontinuity in the regular structure, and that the causes of the reaction may be dependent upon contact between the pair of solid phases concerned. This is analogous to the fact that a perfect crystal of a substance which normally would effloresce may remain unchanged but begin to effloresce as soon as its surface is scratched. We meet the same phenomenon in cases more usually regarded as cases of corrosion, corrosion being much more likely to occur at irregularities of any kind in or at the surface of the metal, even if the irregularity is a grain of so inert a substance as sand resting on the metal. This leads one to wonder if we should not look upon the break in regularity of the surface as the occasion both of the corrosion and of local potential differences, upon the latter as a symptom rather than as a cause of the disease. To the writer it seems advantageous to refer the phenomena directly to the surface even though this, in a sense, is to try to explain one unknown in terms of another unknown. At least, it emphasizes the necessity of further and more thorough investigation of surface films on metals.

As to the value of more definite knowledge of the mechanism of corrosion, little need be said. We are hardly likely to be able effectually to minimize the losses due to corrosion until we have a better understanding of its mechanism. This loss is enormous, for an appreciable fraction of the metal produced each year is used to replace metal rendered useless by corrosion. Consequently, the return from even a partial answer would soon repay the cost of investigation. There is an increasing willingness to consider the problem as a whole, instead of merely attempting to find a way of obviating some particular difficulty, and recent work has thrown light on many places which were dim or even dark. Many committees are interested in different aspects of the matter, and an effort is being made to bring together these various viewpoints. There is, however, no lack of opportunity for the investigator who has an idea and opportunity to try it out.

Society Meetings with Exposition

The Chemical Exposition this year is being held as usual during the week following the annual meeting of the AMERICAN CHEMICAL SOCIETY at Milwaukee. Immediately after the close of the meeting its members will entrain for New York in order to spend the week of the 17th at the exposition. The usual meeting of the American Ceramic Society will be held in conjunction with the exposition in the Grand Central Palace on September 19, probably extending over several days. The annual banquet and election of the Salesmen's Association of the American Chemical Industry will also be held during this week, probably at one of the Pershing Square group of hotels near the Grand Central Palace. The regular dinner of the American Institute of Chemical Engineers will be on Wednesday evening, September 19, at the Park Avenue Hotel, reservation for which should be sent to John C. Olsen, secretary, 85 Livingston St., Brooklyn, N. Y.

Recent Contributions of Chemistry to Medicine

By Ernest H. Volwiler

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MEDICINE as an art is gradually giving way to medicine as a science, but the process is a slow one which can never be completed, for the successful physician must be somewhat of an artist in his work, as well as a keen scientist. The transformation toward the scientific side has been considerably accelerated during the last twenty years, owing largely to the application of many of the principles of the various branches of chemistry and physics, which the medical profession has gladly accepted and wisely employed. Biochemistry, with the related branches of science that it involves, is the key to the door through which most modern success in medicine is being obtained, and the information which it has placed at the disposal of the physician has led to marked changes in the types of substances which he administers.

E. H. Volwiler

The history of drugs and their use indicates many substances which are nearly if not quite as toxic to the host as to the parasite. One service which modern chemistry is rendering consists in replacing the old, crude, "shot-gun" mixtures by compounds which, although still somewhat toxic, are limited in action to a few specific effects that are fairly well understood. Practically every drug in use to-day is to some extent a poison; to speak of a drug as being "nontoxic" is to ignore the fact that the therapeutic effects of substances cannot be limited strictly to the conditions which it is intended to relieve or to the destruction of an invading organism—there certainly will be side effects which will affect more or less undesirably the healthy, normal tissues. The end in view, but not the path to follow, is usually well defined; the therapeutic efficiency must be raised to the utmost, and the side effects eliminated as nearly as possible.

It must be admitted that the present state of our knowledge of the maintenance of health and the treatment of disease is still quite unsatisfactory. Even after the diagnosis of a disease has been correctly made, the remedy available for its treatment is often ill-chosen and unsuited. In the final analysis, the actions of all drugs must be referred to the cells themselves, concerning whose nature and reactions our knowledge is very fragmentary. Owing to the cells' complex structure, there can be but little hope that it eventually will be possible to express the action of most drugs in terms of definite chemical reactions; but it is perhaps not beyond our reach to determine why particular compounds exert certain actions upon the cells, and how these actions may be enhanced or retarded.

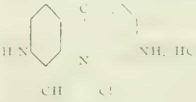
Recent years have brought about some important advances in the treatment and prevention of disease. A few of these will be briefly sketched in the following paragraphs.

DYES IN MEDICINE

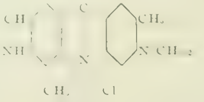
In the last decade probably no other series of substances has shown more promising progress in the therapeutic field than dyes, which have been found to have a wide application, first as reagents in bacteriology, and later in the clinical treatment of disease. As early as 1887 certain dyes were found to possess bacteriostatic action, but it was not until 1912 that Churchman,[1,*] and later Simon and Wood[2] began a systematic study of these compounds. It was found in the rather extensive series investigated by them that the triaminotriphenylmethane dyes possess the greatest antiseptic or bacteriostatic action, and that this is dependent upon the auxochromic amino group as well as upon the triphenyl nucleus itself. Acid dyes are in general much less effective than basic dyes, and the effect of alkyl groups is uncertain. A much greater variety of dyes has recently been studied by Browning and Cohen[3] and by Norton and Davis.[4] Their work indicates the need for much more study, for we are as yet unable to determine what nuclei or groups are essential for the production of antisepsis. Among the dyes which have proved most efficient toward the pneumococcus-streptococcus group of bacteria are brilliant green, gentian violet, and crystal violet. The successful cure of pneumonia has yet to be discovered, and it is not unlikely that such work as this may lead to the successful solution of the problem.

It is in the treatment of syphilis and gonorrhea that dyes have been most extensively investigated. Ehrlich and his collaborators studied the use of trypan blue and of acriflavine as specifics for syphilis, but the results were not particularly encouraging. It was later found,[5] however, that acriflavine (trypaflavine) is almost unique among bactericidal agents, inasmuch as its action is enhanced in the presence of serum, instead of being retarded. This led to its extended use as a remedy for gonorrhea, particularly in Great Britain and America. Incidentally, it is said that during the war acriflavine was almost universally used in the German army in the treatment of wounds.

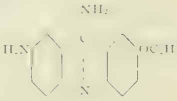
The success of acriflavine has naturally led to the synthesis of a great many modifications of it; only two, which were developed in Germany, need be mentioned here—



ACRIFLAVINE



FLAVIZID



RIVANOL

namely, flavizid and rivanol. Rivanol was discovered by

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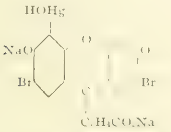
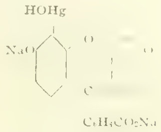
* Numbers refer to bibliography at end of article.

Morgenroth[6] who is noted for his work on quinine derivatives for the treatment of pneumonia. It appears valuable in the treatment of streptococcic infections, although the work with both it and flavizid is too incomplete to justify final judgment as to their true value.

American investigators have begun work in some interesting and altogether new series of dyes, which are of importance inasmuch as they may lead to other even more valuable compounds. Two phthaleins containing mercury, mercurochrome-220 and flumerin,



MERCUROCHROME



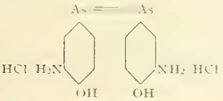
FLUMERIN

have been studied by White and his collaborators.[7] Mercurochrome is being employed as a general antiseptic, while flumerin has been suggested for use as an antisyphilitic. Sodium-*p*-hydroxymercuri-*o*-nitrophenolate (mercurophen), investigated by Schamberg, Kolmer, and Raiziss,[8] has proved valuable as a general antiseptic.

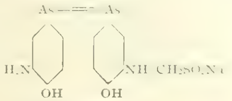
There can be no doubt that the use of dyes in medicine constitutes an important step in the evolution of modern therapeutic measures, but they will be superseded as soon as other non-dyeing compounds of equal or greater efficiency can be developed. In the present state of bacteriological and clinical knowledge, the staining qualities of dyes give a good method for following their action, but indications are not lacking that there are other substances which do not possess the objectionable dyeing or staining qualities, but which, nevertheless, may be equally efficient.

TREATMENT OF SYPHILIS

Eternal vigilance and most vigorous therapeutic measures constitute the only hope of eradicating or even controlling syphilis, which is to-day probably the world's greatest scourge. It is interesting to note that mercury was used in its treatment almost from the time of its appearance in Europe, but mercury in its varied forms has up to the present proved at best a rather dangerous drug to employ. Probably no advance in medicine has exceeded in importance the discovery of the arsphenamines by Ehrlich in 1910. Ehrlich's work constitutes the first extended investigation in the field of chemotherapy or the correlation of chemical constitution and physiologic action to produce specific desired therapeutic effects.



ARSPHENAMINE



NEOARSPHENAMINE

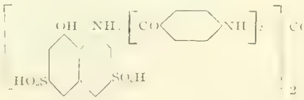
It seems probable that if the persêverance and care taken in the development of these compounds of arsenic were to be applied to the study of other diseases, a number of them would be passing into the category of rare maladies. On account of the prevalence and difficulty of control of syphilis, however, it cannot even be stated that it is on the decline; but the use of the arsphenamines has assuredly been of great value in checking its ravages.

An immense amount of research has been carried on in all civilized countries during the last decade in the attempt to develop products superior to the arsphenamines, but up to the present the main progress, in which chemists of the United States have had a most prominent part, has come in decreasing the toxicity and increasing the safety of the arsphenamines, rather than in the discovery of new compounds in other series. Recently Voegtlin[9] has focused attention upon sulfarsphenamine, one of the compounds related to arsphenamine, prepared by Ehrlich and his collaborators, but apparently discarded by them. Since it is a bisulfite derivative instead of the sulfoxalate compound (neoarsphenamine), it is less susceptible to the formation of toxic oxidation products and is giving promise of some valuable therapeutic application.

Jacobs and Heidelberger,[10] in an admirably systematic series of investigations, have developed the sodium salt of *N*-phenylglycineamide-*p*-arsonic acid, called tryparsamide, which has proved valuable in the treatment of African sleeping sickness, a trypanosome disease related to syphilis. The compound was deemed of little value in the treatment of syphilis, partly because of the danger of producing blindness, but recent clinical experiments indicate that it may have a place in the treatment of neuro-syphilis, a form of tertiary syphilis. It may also be said that sulfarsphenamine has very recently given promise in this same field.

Although arsenic administration for syphilis has held the limelight, the simultaneous or separate use of mercury has by no means been abandoned, and other metals are finding use. Apparently, the arsphenamines clear the blood stream of the spirochetes with remarkable rapidity and the simultaneous use of mercury preparations prevents the organisms from finding lodgment in the tissues. Recently disodiummercurisalicylacetate (mercurosal) has been placed upon the market as an antisyphilitic. A number of investigators, particularly in American universities, aided and encouraged by the United States Interdepartmental Social Hygiene Board, are carrying on important work with mercury compounds. Moreover, bismuth compounds, for example, sodium potassium tartrobismuthate, introduced by French pharmacologists and physicians, have attracted a great deal of attention, particularly for use in those cases where arsenic and mercury are not well tolerated or where they are ineffective. In efficiency, compounds of arsenic, bismuth, and mercury are said[12] to bear the approximate relative ratio 10:7:4.

The most promising treatment of trypanosome diseases, such as syphilis and African sleeping sickness, has heretofore seemed to involve the administration of compounds of metals, such as arsenic, but the recent work in Germany indicates that eventually purely organic compounds may be equally promising, if not even more so. Owing to the conditions brought about by the war, the nature of these substances has been carefully guarded, but they are apparently complex aromatic amides synthesized from naphthalenesulfonic acids, phosgene, and nitrobenzoic acid, or similar intermediates:



BAYER-205 (possible formula)

"Bayer-205" appears to be of value in the treatment of African sleeping sickness, but is apparently not applicable for use in human syphilis.

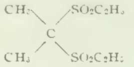
It is interesting that the immense amount of excellent work which has been done by scores of investigators of many nations, with good facilities at hand, has produced comparatively little aside from advances in the production of the arsphenamines of high quality and potency. Nevertheless, a broad and sound basis is being laid from which we may reasonably expect to develop the "lucky accident" that will constitute the next big step in our progress toward the elimination of syphilis. Whether this advance will come along the line of purely organic compounds, or whether compounds of metals such as arsenic will continue to be the best remedies, cannot at present be predicted.

Hypnotics and Sedatives

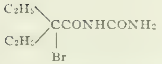
It cannot be said that the power of producing sleep is inherent in any certain combination of groups, inasmuch as there is a wide variety of nuclei, both inorganic and organic, which may form the basis of hypnotic compounds. Most modern hypnotics belong to the organic series; among the first of these to be used was chloral hydrate. Other products which have come into use are based upon the nuclei of urethane (I, VIII), sulfonmethane (II), halogen-substituted acid ureides (III), pyrimidine (IV), hydantoin (V), homophthalimide (VI), and diketotetrahydroxazole (VII).

$NH_2COOC_2H_5$

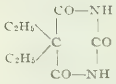
I—Urethane



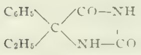
II—Diethylsulfonedimethylmethane (Sulfanol)



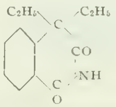
III—α-Bromodiethylacetylurea (Adalin)



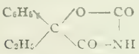
IV — Diethylbarbituric Acid (Barbital, Veronal)



V—Phenylethylhydantoin (Nirvanol)



VI—Diethylhomophthalimide[13]



VII—Phenylethyldiketotetrahydroxazole[14]

$NH_2COOCH_2CCl_3$

VIII—Trichloroethylurethane (Voluntal)[15]

An examination of the structures of these compounds indicates that their activity is based upon the presence of one or more of the following atoms or groups: (1) alkyl groups, (2) halogen atoms, (3) ketone or aldehyde groups. Nevertheless, there are so many factors involved and the compounds show such wide variations in activity that a correlation between their constitution and their sleep-producing properties is still impossible. Urethane and voluntal are mild in action, of low toxicity, and require to be given in comparatively large doses; whereas the others are stronger in action and more toxic, but are effective in smaller doses. The sulfonmethane series (sulfonal, trional, and tetronal) was at one time extensively used, but the compounds were found to have deleterious action upon the heart and other organs. Probably no hypnotic has ever come into as extended use all over the world as barbital. Since some new alcohols have recently become available, other dialkylbarbituric acids have been prepared and of these the *n*-butylethyl and the isoamylethyl compounds seem to be best, exceeding by several times the activity of barbital itself.[16]

Apparently, the investigations of hypnotics have not been correlated closely enough with the physico-chemical methods available for testing and comparing the products. Over twenty years ago Overton[17] and Meyer[18] showed that in a given series there is a more or less close relationship between physiological activity and the partition coefficients of the compounds between fats and water, and they illustrated this relationship by experiments upon a number of hypnotics which were known at that time. The physiological testing of hypnotics is not always entirely satisfactory and no doubt this difficulty could in some cases be overcome by simultaneously carrying out physico-chemical tests as suggested by Overton.

If a physician were asked to choose the most valuable single drug at his disposal, morphine would probably be his choice. This drug has a host of uses, one of which is as a hypnotic. The elucidation of the structure of morphine has been the object of an immense amount of work, particularly by Knorr, Pschorr, Freund, Vongerichten, and more recently by Gulland and Robinson,[19] but even to-day we are not quite sure of the structure of certain portions of its complex molecule. Morphine is a dangerous drug to use, not only because of its toxicity, but also because of the degrading habit formation which it induces. Doubtless some portions of the molecule of morphine are useless and harmful, and it is most likely that it is possible to synthesize more simple organic compounds which would produce the effect desired without the drawbacks inherent in the naturally occurring alkaloid. Cocaine is being gradually replaced in this manner by synthetic local anesthetics, and the value of a similar substitution for morphine would be inestimable.

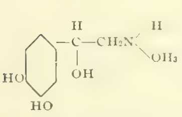
Surgical operations cannot usually be performed under the ordinary hypnotics in doses in which they may be safely employed. What would be desirable is a safe hypnotic which, while producing a natural sleep in which the normal body functions are undisturbed, will at the same time render the patient insensible to pain. It is not unlikely that in the realm of synthetic chemistry some day will be discovered a product which more closely approximates the ideal hypnotic anesthetic.

Benzyl Esters

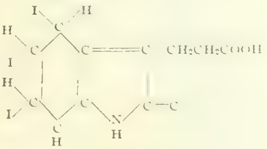
Few better illustrations of how the chemist proceeds in his attempts to discover the physiologically active nucleus of a naturally occurring drug, and then follows it up by synthesizing a more simple and effective substitute, can be had than the development by Macht[20] of the use of benzyl esters to relieve the pain caused by the rhythmic contractions of involuntary muscle. Papaverine, one of the alkaloids of the opium group, contains a substituted benzyl radical, and reasoning from this fact, Macht investigated the action of simple benzyl esters, such as the benzoate. They were found to possess an action similar to that of papaverine, less complicated by undesirable side actions, and the products are cheaper than papaverine. This discovery was soon followed by the introduction of a large number of other benzyl esters, such as the succinate, stearate, fumarate, phosphate, acetylsalicylate, etc., all of which possess more or less important advantages over the benzoate. It was soon discovered by Wildman,[21] however, that benzyl ethers produce the same relaxant action on smooth muscle, and recently Kamm[22] has indicated that the effect exerted by benzyl compounds is not specific for the benzyl group, but that other more or less unrelated radicals produce the same action. The value of benzyl compounds in medicine has by no means been definitely decided. Hailed at first by many of the uninformed as being perfect substitutes for not only papaverine but for morphine also, they have in many cases proved disappointing and their use has now practically fallen into certain well-defined channels, where only extended clinical application can finally determine their true value.

Naturally Occurring Products

The lack or superabundance of certain substances occurring in the body may produce most profound changes and abnormalities in our well-being and physical appearance. These substances usually occur in very small amounts in the various glands of internal secretion, and, in general, little is known concerning either their mode of action or their chemical identities. Epinephrine (adrenaline), the blood-pressure raising constituent of the suprarenal glands, is better understood chemically and physiologically than any of the others. Its structure is definitely known, owing to the painstaking and excellent investigations of three chemists in America—Abel, Aldrich, and Takamine—and not only is the pure naturally occurring product available, but its synthesis has been solved and the synthetic product is now used by physicians side by side with the epinephrine obtained from suprarenal glands. Nearly all the analogous products which have been synthesized are much less active or are entirely inactive, but it has recently been stated that an analogous naphthalene derivative is forty times more active than epinephrine itself.[23]



Epinephrine (Adrenaline)



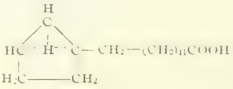
Thyroxin

To Kendall[24] we owe the greater part of our rather extended knowledge of the active principle of the thyroid gland. It is well known that a deficiency or excess of this active constituent produces the most marked effects, not only upon the health of an individual, but also upon his physical characteristics. Certain localities, such as Italy, Switzerland, and our Great Lakes region, show a remarkable prevalence of certain diseases, often goiter, and it has been shown that the water in these communities is deficient in iodine. Kendall and his collaborators by their remarkable work have not only isolated the pure active substance (thyroxin) of the thyroid and indicated its structure, but they have made good progress toward its synthesis. Some of the difficulties encountered may be imagined when it is noted that the thyroxin molecule is not only quite complex in itself, but also contains several asymmetric carbon atoms. When this problem is solved, it will be of interest to determine what portions of the molecule are actually essential; that iodine must be present is certain.

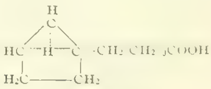
Our knowledge of the products occurring in the other glands of the body is also far from being complete. The tiny pituitary body, lying at the base of the brain, is the source of a blood-pressure raising substance which has long been in use to control hemorrhage, etc. Abel[25] at one time believed that histamine (4-imidazolylethylamine) occurred in some combination to constitute the active principle, but this belief seems no longer tenable[26] and we are almost as much in doubt as ever as to its true nature. The successful solution of the problem promises ample reward to the investigator who can accomplish it.

Probably no discovery since that of the arsphenamines has attracted so much immediate attention as that of insulin, used in the treatment of diabetes. Here again the long and painstaking labors of many biochemists needed only the final touch of a keen investigator to make a needed and valuable product available—this touch being supplied by the Canadians, Banting and Best[27] and their collaborators. Insulin is obtainable by the careful and rather complicated extraction of the Islets of Langerhans, small bodies which exist in conjunction with the pancreas and which are intimately concerned with the metabolism of sugar. By daily injection of a solution of insulin even hopeless cases of diabetes may be so relieved that the patient can return to a fairly normal existence. Not only are we ignorant of the composition of insulin, but we do not even know whether the active constituent is a protein or not. Scores of biochemists have labored diligently with it during the last two years, but their efforts have tended mainly toward the isolation of a fairly pure and safe extract; the surface of its chemical investigation has not even been scratched.

To these few naturally occurring therapeutically valuable products can be added a host of others, and we know far too little about any of them. The vitamins are almost as much of an enigma as ever. Digitalis is used daily as a heart stimulant, as is strophanthin, but their chemical natures cannot at present even be inferred. Morphine has already been mentioned, but of most of the alkaloids we know far less than we do of it. An interesting development in the treatment of leprosy has come through the use of salts or esters of the acids of chaulmoogra oil, obtained from the seed of a tropical tree. Leprosy is a disease to which lower animals are not susceptible and the investigations of its cure in man have lagged because proposed remedies could not be pharmacologically tested. It is not claimed that the salts or esters of two of the acids of chaulmoogra oil—namely, chaulmoogric acid and hydnocarpic acid—are really satisfactory for the treatment of leprosy, but they represent the best means at present available. These acids differ from any previously known fatty acids in containing a five-membered carbon ring. The dotted lines in the formulas indicate that the points of attachment of the bonds are unknown.



Chaulmoogric Acid



Hydnocarpic Acid

Conclusion

The foregoing brief discussion includes only a few of the types of substances employed in medicine. There are, of course, many other series which have found application for specific purposes in medical practice, and the chemical and physiological problems connected with them are just as important and needful of solution as any of those indicated in the foregoing discussion. The tendency, of course, is to press on to discover products of therapeutic value in new fields, but the old ones must not be abandoned until our knowledge about them is far more complete than at present. The practice of medicine can be placed upon a more rational basis by a clearer understanding of the relationships existing between chemical constitution and physiological action, and a closer coöperation between the chemist, pharmacologist, bacteriologist, and clinician. It seems that endowed institutes for chemico-medical research, such as the Rockefeller Institute in New York City, have the greatest opportunities for performing the fundamental research necessary to lay a sound basis for future progress. Until there is such a basis, there will always be products introduced on the market which should never be there, and other products of real value will be passed by without real trial. As recently pointed out by Hirschfelder, coöperation by the manufacturer is needed so that leads suggested by the pharmacologist may be properly utilized; but equally important is the need of obtaining complete pharmacological tests of substances which have been prepared by the chemist, and which frequently languish and slowly die because their therapeutic value has never been definitely decided.

Beside the advances along the lines already explored will come investigations in new channels. The armamentarium of the chemist has not only been strengthened by new organic compounds, such as the new alcohols now commercially available, but theoretical chemistry is continually placing at his disposal new methods for producing substances which neither nature nor man has previously employed. What we may expect in the future in the treatment of disease is measured by the industry, resourcefulness, and coöperation of those concerned.

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Note on Quantitative Büchner Filter[1]

By R. J. Cross

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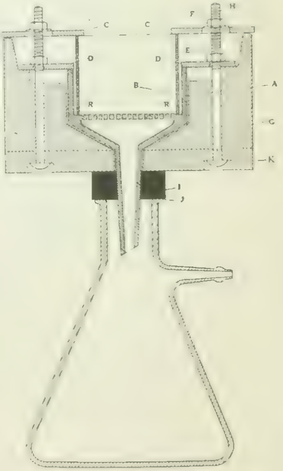
THE quantitative Büchner filter herein illustrated was designed for use in filtering and washing the phosphotungstic precipitate in the Van Slyke nitrogen distribution determination. However, it has proved so convenient in filtering and washing other bulky precipitates with a mimimum of solution that separate mention is here made of it. The chief improvement lies in the use of a retaining glass or porcelain cylinder, *B*, which holds the filter paper down firmly on the grid of an ordinary Büchner funnel, *A*. The ground joint at *R* is made by using as a blank a metal cylinder, preferably of cast iron, whose end has been faced off in a lathe. The exterior diameter of this blank is larger than that of the cylinder *B* and its interior diameter smaller. The annular channel at *R* is cut by applying a little carborundum and water, and rotating the blank back and forth. This material cuts the porcelain quite rapidly, and it only requires a few minutes to produce a true surface all the way around. The end of the retaining cylinder *B* is ground true in the same way.

In the smaller sizes, especially, it is convenient to make the wooden base, *K*, wide. The filter may then be supported on an iron ring, and all danger of its being upset removed. Upon completing a filtration the nuts, *F*, are loosened and clamp *C* slid back from *B*. A watch glass or other retainer may then be placed over *B*, and the whole filter inverted. By blowing through the stem of the funnel the filter and contents are loosened from the grid and are quantitatively removed with *B*.

Attention should be called here to the added convenience in using flat joints, as at *J*, instead of the usual ring or rubber stopper. The pressure being downward, a joint of this kind, of rubber on glass, is easily made quite tight, whereas much time is often wasted in trying to make rubber stoppers tight. Further, the suction flasks found in the average laboratory are a miscellaneous lot—no two alike—but, if they are all ground flat on top, any filter may be used with any funnel.



VERTICAL CROSS SECTION THROUGH QUANTITATIVE BUCHNER FILTER

The writer has also made many vacuum distillations and has found that the use of flat joints with rubber gaskets has greatly facilitated the work owing to absence of leakage.

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[1] Received August 13, 1923.

Chemistry in the Control of Plant Enemies

New Achievements and Future Possibilities

By **Walter Collins O'Kane**

Crop Protection Institute, Durham, N. H.

NOTHING is more important in human welfare than protection from the myriads of minute enemies in the plant and animal world. In this chemistry is now taking a leading part and is certain to make extraordinary development.

Walter Collins O'Kane

By the very nature of the case this must be so. The whole tendency of man is to flock together, to subjugate the living world and make it yield sustenance, shelter, and all else. In vast areas this has been going on for hundreds, or even thousands, of years. In other wide spaces it is only beginning. The tendency is as strong as human nature itself, and it is constantly assuming concrete shape.

So it is that the human race is the great upsetter of the natural balance in nature. We cut down forests, pull out the stumps, plow the land, and plant a hundred thousand acres of potatoes. We break up the sod of a million acres of prairie and seed it all down to wheat.

All this is necessary and, apparently, is going to continue and to increase. The same number of acres that supported a man and his family must come to support a score or a hundred, who are working to make other things that the man and his family, and many others besides, want and need.

We cannot do this and expect natural forces to protect from harm the altered conditions that we have brought about in our fields and gardens. A microscopic organism that would cause a rust spot on a wheat plant might blow about in the wind and never find a suitable plant, if wheat grew only as single, isolated specimens, scattered here and there in the midst of other vegetation. But that same microscopic organism developing on a plant in a thousand-acre Dakota field cannot fail to find a suitable host on which to develop. A beetle with black and orange stripes, hunting for wild potatoes in mountain highlands, may find the chances a thousand to one against it. But the same beetle in a Michigan potato field needs a dose of poison to put an end to its career.

The increased price of a product is bound to make it possible to spend money to raise it successfully, if it is something that human beings need, or want, or think they want. There is no more doubt about that than there is about the rising of the sun to-morrow. And it is quite certain that the demand for foodstuffs with which to support life, for the products that make life pleasurable, and even for those that bring luxury, is not going to fall off.

The means of avoiding losses from the various minute enemies can take many forms. At the beginning the methods are sure to be crude and laborious. The owner of the potato patch goes through it with a stick in his hand, knocks the potato beetles off onto the ground, and tramps on them. But presently he carries a pail with him as he goes down the row, pours a cupful of kerosene into the pail, and knocks the beetles into this improvised device where the touch of a drop of the liquid will finish off the pest, thus saving time and energy and rendering his task more efficient. He has turned, as he should, to chemistry.

It is a long step from this crude process to the spraying, dusting, and fumigating that are now helping us to raise crops. But it is not a long step in time. The last twenty years have seen the greater part of the development, and a period much shorter than that has witnessed a large proportion of the more important discoveries. The field is relatively new, as work in chemistry goes, and the progress that has been made is only a fraction of that which has been achieved in other lines where the demands of industry on the resources of the chemist were stronger.

Within these few years striking advance has been made and materials have been developed that not only are important in themselves, but may rightly be taken as forerunners of the progress that is sure to follow. It is interesting and suggestive to consider some of these developments.

p-Dichlorobenzene for Peach Borer

Take the peach borer, for example. There has been hitherto no satisfactory control of this pest. Recent work in New Jersey has shown that p-dichlorobenzene, applied in a ring near the trunk of the tree and covered with soil, affords efficient and economical control. Several hundred thousand trees have now been treated through two or three seasons and the method is a proved success. Other possibilities of the substance are now being studied.

Sulfur Sprays

Sulfur was one of the first elements ever to be used for the control of plant diseases. Within the memory of most of us a chemical combination of sulfur and lime came into use as a spray to kill scale and to help control certain fungous diseases. But nobody knew precisely how the thing worked. It would act in certain fashion under one set of conditions, but in other manner under other circumstances. It was like a rifle that could shoot a bullet a long distance, but could not always be aimed, and sometimes missed fire.

Within the year much of this mystery has been cleared up and a possible means of controlling and enlarging the utility of sulfur has been discovered. It has been found that in the changes that lime sulfur undergoes after it has been applied as a spray, a new substance is formed which is the really active agent in control of plant diseases. Furthermore, ways have been found which promise to make it possible to control the formation of this substance and at the same time to take lime sulfur out of the class of sprays that burn foliage and place it in the class of those that can be used quite safely in large amounts and in heavy concentration.

Sodium Fluoride for Roaches

Among the oldest of insect pests, as the geologists measure time, are the roaches. Prehistoric man may not have stayed long enough in one place to be bothered by them, but we know that they were in existence in those remote times quite as abundantly as they are now. There have been hundreds of roach powders, pastes, traps, and cures. Some of them do more or less good. But recently we have found in sodium fluoride a material that, rightly used, can eliminate roaches from overrun premises. The same material will kill ants. And so, probably for the first time in history, the human species can easily and securely rid itself of two prize nuisances in the insect world.

Possibilities of Mercury

Plant pathologists are well aware that in handling certain plant organisms in the presence of mercury they must protect them from the effects of its vapors. To what extent can this properly be utilized? How about its effects on animal organisms, such as insects? In parts of India there is a tradition that mercury, exposed in a tight container along with beans or other stored products on which the bean weevil has laid its eggs, will prevent these eggs from hatching. American experimenters have put this tradition to the test in recent trials and have found that the mercury does have a definite effect. The volatilization of the mercury is presumably very slow. A chemist's balance would have difficulty in detecting the loss, except by exceedingly delicate measurements.

Control of Cereal Grain Smuts

The smuts of cereal grains have offered a serious problem to the expert in plant diseases. There was no mystery about the cause or the way in which they were carried. The difficulty lay in proposing a means of control that would be practical on a large scale. Two new measures are among the recent discoveries. The first of these turns to copper, a metal that has long been utilized in one way or another in fighting plant diseases. The other lies in the group of organic mercuric compounds that have been developed since the beginning of the World War.

New Uses for Carbon Disulfide

Carbon disulfide, used for many years as a fumigant for grain weevils, is yielding new facts as a result of further study, backed by vision and resourcefulness. An experimenter, finding mosquito wrigglers abundant in a tub of stagnant water, dropped into it a teaspoonful of carbon disulfide. One would not expect any marked results, since the material is not soluble in water, except in slight degree. But in a minute or two the wrigglers were in discomfort and in a few minutes more they were dead. The instance is suggestive. Other experimenters have tried an emulsion of carbon disulfide, greatly diluted with water, as a possible material for killing grubs at work on grass roots. Curiously, they have found that moderate amounts of the material, thus emulsified and diluted, bring about a high percentage of kill.

Insect Baits and Repellents

We have only begun to explore the possibilities that may lie in the use of chemical compounds as baits for noxious insects, or as repellents. Every insect is a bundle of automatic reactions. Most of all, it is attracted or repelled by odors. This response largely controls the movement of an insect in search of food and, therefore, has a great deal to do with its harmful activity. If we can place before it an effective poison and can add to our dose some compound that will prove sufficiently attractive, we may persuade the pest to partake of our offering. Perhaps we can attract it away from the plant or product that it would injure in its feeding, and persuade it to eat something that is valueless while at the same time working its own destruction. Thus, amyl acetate has been found to serve as an attractive ingredient in a poison bait for grasshoppers.

But that is only a beginning. The corn-ear worm has a wide range of food plants. The adult that lays the eggs from which the worms hatch is attracted by corn silk. Investigators have taken strands of cotton twine, soaked them in the juice obtained by crushing corn silk, and have attracted the moths to these strands. By studying the composition of the silk, isolating the active principle that attracts the moths, and then seeking the aid of chemistry to devise a substance that will simulate this principle, it may prove possible to devise a poison bait for this destructive pest that will protect our vast cornfields from the tremendous damage that they now suffer because of it. If this can be done, as appears not at all impossible, we may be able to follow a similar procedure with reference to many other devastating pests.

But the work and the possibilities do not end there. What shall we use as a poison? For many years our principal reliance has been placed on arsenic in one or another of its compounds. But we have reason to believe that the toxicity of various arsenical compounds to insects is by no means in direct proportion to the amount of arsenic that the compounds contain. Work is now in progress which is intended to throw light on this question, to help us to learn what forms of arsenic become most toxic within the digestive tract of insects and what influence may be exerted by the physical character of the material.

We have observed, at times, that some insects appear to be repelled by the presence of arsenical poisons on the plants on which they were feeding. Recent work with a new invader, the Japanese beetle, goes to show that so far as this insect is concerned the repellent effect is probably due to the discomfort caused by the irritating character of the first minute amounts of poison eaten. Investigators have tried the experiment of administering with the poison spray an intestinal sedative, such as bismuth subcarbonate. Beetles fed on this mixture ate more of the poisoned leaves; more of the beetles consumed a fatal dose. Administration of bismuth subcarbonate on a large scale would not be practicable. But the principle involved is interesting and important.

Control of Thickness of Spray

There is a big question, which experimenters are only beginning to touch on, that involves the addition of neutral or subsidiary materials to a spray in order to render it more effective through altering its physical qualities. With their assistance it may be possible to control, not only the covering qualities of a spray, but the thickness of the film deposited and its adhesive qualities. Conceivably, we may come to say, before long, that protection of apple foliage from a certain invading plant disease will require a film so many microns in thickness persisting through so many days, that less than this will be ineffective, and that more will be a waste of material.

Effect of Mixtures

Most of our spray schedules nowadays call for mixtures of this or that. We need to apply materials that will accomplish more than one purpose and it is highly advantageous to do this in one operation. However, this turns the spray barrel into a chemical laboratory. Because Ingredient *A* is effective for one purpose and Ingredient *B* for another, it does not follow that *A* and *B* mixed together will retain their valuable characters in full degree, or even at all. They may, instead, gain a new character that makes them highly harmful. The sprays to be worked out for the future must be devised, not only with reference to their individual qualities, but with reference to their compatability one with another.

Unsolved Problems

In many of the new fields of inquiry we cannot even lay claim to a good start. Early blight once started in a potato field can, and sometimes does, sweep through it so rapidly that the ordinary grower, aware of the existence of the disease only when it has gained headway, cannot stop it before it has utterly destroyed his crop. The plant pathologist, taking it in time, can spray and check it. But what can we offer the grower that will prevent infection?

A recent list prepared by a committee of plant pathologists gives more than a hundred plant diseases carried by seeds. More than fifty of these are endophytes living within the substance of the seed. Some of these diseases take enormous toll of our crops. How shall we treat seeds on the large scale in which they must be handled in farm practice and sterilize them successfully?

Investigators have worked diligently to discover the cause of the mosaic diseases affecting various plants. We do not yet know what the cause may be. Without this knowledge we are badly handicapped in our search for means of control.

In certain sections of the East a serious plant enemy has become established, known as the potato wart disease. About the only recommendation that can be offered the grower is to change to varieties of potatoes that have been found to possess more or less resistance. We need to discover a definite and specific means of solving this and other equally unsolved problems.

Nine times out of ten, perhaps ninety-nine times out of a hundred, our constantly increasing reliance in all this must be placed on discoveries in chemistry, working in intimate alliance with the biological sciences, with plant pathology, entomology, and bacteriology. It is an enormous field and the possibilities are equally tremendous.

Using Excess Power to Save Coal

Electrical Generation of Steam for Heating and Process Work

By E. H. Horstkotte

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OFF-PEAK periods of demand for power on idle days when plants are shut down and Sundays and holidays often present important problems in fuel economy to plant engineers who are obliged to keep steam on the system for heating or other purposes. Heretofore, it has been necessary to keep at least one fuel-fired boiler in action, with the attendant expense of firemen, to say nothing of the fuel consumed. Textile mills, chemical plants, manufacturers of pulp and paper, and other industries, including central stations from whom such plants purchase power, if they do not make it themselves, are alike affected by this problem.

Description of Generating Plant

The recent development of practical and economical means for the electrical generation of steam is affording an interesting solution to this problem of fuel economy through the use of an electric steam boiler which in effect may be said to form a complete steam-generating plant capable of operation with minimum attendance.

The complete equipment consists of the shell with supporting feet, the electrodes, insulators, steam and water gages, safety valve, circulating pump and motor, and a panel on which is mounted the control equipment (Fig. 1).

The tank, or generator shell, is mounted vertically, and divided horizontally into two compartments, the upper known as the electrode compartment, where the actual generation of steam takes place, and the lower forming a self-contained hot well. Water entering the hot well from the feed-water pipe is forced into the upper chamber by a motor-driven centrifugal pump located on a short external pipe line. From this chamber it flows back into the hot well through a number of small holes on the outer circumference of the dividing plate. This arrangement provides a continual circulation of heated water, the water level in the electrode chamber being held at the desired level by setting the valve in the circulating pump discharge line.

The upper, or electrode chamber, where the steam is generated, contains three large, round, iron electrodes rigidly supported from the roof, the current-carrying supporting rods coming in through specially designed insulating bushings. These bushings are provided with a small duct in the top leading to the outside air. Thus, if steam does succeed in leaking through the packing into the upper section of the bushing, it passes out freely instead of creating a pressure that might blow out the side of the insulator.

The electrical operation resembles that of a three-phase arc furnace. Normally, the electrodes are submerged in the water, and the three-phase current passes through the water to the sides of the tank, or from electrode to electrode. The steam is generated by current flowing through the water, which is of high resistance. The temperature of all the water in the system is practically uniform. If the steam pressure lowers owing to an increased demand, rapid steam generation due to the high temperature of the water and the degree to which the electrodes are submerged quickly brings the pressure up again.

Another operating feature is that since the water level is maintained by the adjustment of the throttle of the circulating pump, the energy consumption of the generator is not dependent on the operation of the feed-water pump. The supply of water in the hot well is regulated by an automatic feed-water regulator. Furthermore, when it is desired to reduce the load, the generator does not have to be blown, which means that water does not have to be pumped in subsequently against full pressure. The only energy losses in the circulating pump are the motor losses and the pump and bearing friction losses; therefore, all energy delivered to the pump eventually goes into heat in the water, and there is no wastage.

The control equipment consists of an incoming line panel carrying automatic circuit breakers, necessary meters and instrument transformers, and the control apparatus for the circulating pump. Since the kilowatt capacity of these boilers is comparatively large, the devices used on the board are of the same heavy construction and have the same current-carrying and rupturing capacity as those used for similar duty in substations, heavy feeder circuits, tie lines, etc.

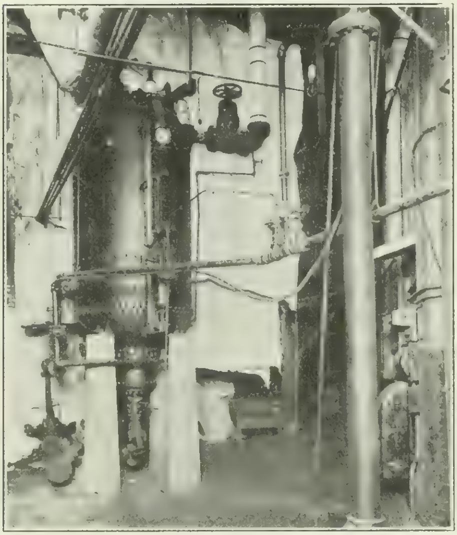

Fig. 1—Electric Steam Generator

Safety Factor

Of vital importance in this, as in all apparatus for the production of steam, is the safety factor. For several reasons, it may be said that the safety factor of the steam generator is even greater than that of the average boiler, highly developed as the latter is. The safety valve takes care of excess pressure, as on the standard variety of boiler, and the method of protecting the insulators has been described. Further contingencies are taken care of by what may be described as the interlocking of the various controls. Suppose, for example, the circulating pump ceases to function from voltage failure or other cause. The water in the electrode chamber simply drains into the hot well, and since the electrodes are no longer submerged, no more steam is generated. On resumption of the pumping, since there is no hot metal surface in the electrode furnace, there is no danger of an explosion similar to that due to a hot crown sheet in a boiler. Moreover, when the water drains out there is no danger of burning any part of the electrode chamber, because when there is no water no heat is generated. Too high a level of the water is prevented by an emergency drain of large diameter the top of which is some distance from the top of the electrode chamber.

Advantages of Generator

A consideration of the steam supply problems of industrial plants has disclosed many cases where the steam generator has proved a valuable adjunct to the plant equipment, either in utilizing excess electric power, formerly wasted, or in providing process steam directly where it is needed. In paper mills there are at least fifty-nine days in the year when the plant is idle; yet, a supply of steam must be maintained for various purposes. In textile mills steam is necessary to heat the plant, when the motors are not running. Ordinarily, this means that a certain amount of steam must be kept up in the boilers and that, in addition to the fuel, necessitates the presence of firemen and engineers over the idle period. The electric steam generator operates practically without attendance, except for a cursory inspection by a watchman, and its use permits the banking of the fires if coal is used, or the shutting down of oil-fired boilers when the plant is idle.

Many mills purchase power on a maximum demand basis, and here the savings effected by the steam generator are just as tangible, but arise from a different cause. Suppose, for example, a factory contracts for 10,000 kilowatts maximum demand. It is possible that, owing to one cause or another, the load factor for the year may be as low as 75 per cent. In such a case 2500 kilowatt-years, or 21,900,000 kilowatts are being paid for but not used. By installing an electric steam generator to utilize this energy the fuel bills would be cut materially, as follows: Assuming a coal-fired boiler with an efficiency of 65 per cent and coal with 13,000 B. t. u. per pound, for every 4953 kilowatt-hours used in the generator, one ton of coal would be saved, or 4421 tons per year. If oil-fired boilers are used, operating at 75 per cent efficiency and using oil weighing 8 pounds per gallon with 18,700 B. t. u. per pound, for every 32.9 kilowatt-hours there would be saved one gallon of oil, or 665,650 gallons per year. These figures are calculated on the basis that all the excess energy would be utilized. If only 75 per cent were so utilized, the savings would still be enough to more than justify the installation of a steam generator.

In addition to these, other possibilities have presented themselves. Central stations have found it of mutual advantage to themselves and their customers to instal and maintain one of these generators in the customer's factory, metering the steam, and charging the customer according to the amount consumed. Industrial plants supplied with power by their own hydroelectric generating stations can use the excess energy available during high water periods to generate steam, and thus save fuel. Another field is in factories needing small amounts of process steam at widely separated points. It would be much more economical to instal a generator at the point of utilization than to transmit steam for long distances from a central source of supply. As time goes on and the knowledge of the advantages of the electric steam generators is more widely spread, doubtless many other uses will be found which are at present undeveloped.

Four installations, totaling 15,000 kilowatts, have been made of this system of steam generation. An interesting feature of operation in one plant has been reported by a user who states that a careful check has shown a saving of between $50 and $60 per day in coal, when the electric boiler was in operation. This plant, which obtains its power hydroelectrically, utilizes excess power available during the high water periods in the spring and fall of the year. Another plant operates the boiler as an auxiliary to the main power plant when excess power is available and also for such operation on Sundays as is necessary.

A 2500-kilowatt unit is being installed in northern New York State for the heating of a number of school buildings from a central heating plant. The electric boiler will furnish steam for this purpose from hydroelectric power.

Purifying Industrial Water

By **D. H. Killeffer**

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WATER is our most important industrial raw material. No industry can operate without using water in some form at some point in its processes. Four general classes of uses may be recognized in which water owes its importance to its solvent action, its high latent heats in steam and ice production, its high heat capacity in heat transfer, and its mechanical properties as in the production of hydroelectric power, the operation of hydraulic presses, and other similar mechanical operations. In the first two of these uses the composition of the impurities present in the water becomes important, and it is with these that the present discussion will deal.

As to its source, water may be classified, in the order of its purity, as distilled, rain and snow, surface water from streams and shallow wells, deep well water, and sea water. Distilled water naturally contains no impurities except dissolved gases, unless carelessly prepared, and hence need not be subject to purifying treatments. Rain and snow waters contain minimum impurities and are the most sought for industrial waters. Unfortunately, supplies of either are too uncertain and too meager to meet the needs of industry. Water from streams and shallow wells generally is of sufficient purity for industrial use. The objections to surface waters are based on the wide fluctuations of both quantity and quality which occur during the course of the year. Their quantity depends upon rain and snow, which are widely variable, and their quality depends upon the character of the soil over which they pass, as well as upon their velocities. In quality, surface waters vary from a close approach to the ideal of rain water to extremely hard, calcareous water in the limestone regions and to extremely alkaline waters in the arid regions of the West. Deep wells are most frequently calcareous in character, although they may vary through wide ranges depending on the character of the rock formations through which they pass. Deep wells and springs coming from great depths possess uniform clarity, with few, if any, exceptions, which property distinguishes them from surface waters that are frequently muddy from excessive rainfalls. Sea water, with which might also be classed some of the western alkali waters, contains principally salts of sodium and potassium with smaller amounts of alkaline earth metals.

In industrial operations four principal points are raised as to the nature of the impurities in water: its freedom from suspended matter, its freedom from dissolved salts of calcium, magnesium, and the heavy metals, its freedom from excessive amounts of salts of the alkali metals and other dissolved matter, and its freedom from permanent acidity—i. e., acids other than carbonic. Upon these points depends the usefulness of water after the question of volume available has been settled.

Suspended Matter

Suspended matter is objectionable wherever water is used, as it clogs pipes, erodes the vanes of turbines, in boilers it becomes a part of any scale that may be formed, and in all washing operations, particularly those involving fibrous materials, it becomes firmly enmeshed in the material washed and prevents the completion of the washing operation. However, in the case of boilers working under variable loads on extremely pure water, the absence of traces of suspended matter may increase priming to an alarming extent. Priming is analogous to bumping in laboratory operations, and results in throwing water into the steam lines through the sudden formation of steam.

Dissolved Salts

The effects of dissolved impurities are so widely different in different operations that they will be discussed in connection with the uses.

Paper Industry—The largest single use of water as a solvent is probably in the paper industry. Estimates placed on this use run into the billions of gallons per day on the basis of the fact that the manufacture of each ton of paper requires from 50 to 200 thousand gallons of water. In order that the paper be up to standard in all respects, it is necessary that the water used be free from the slightest turbidity and from any elements which are likely to produce insoluble compounds with any of the reagents used in the processes of manufacture. Water for paper manufacture must also be free from color and from salts of metals, such as iron, which might produce color in the product. The principal faults which develop in papers made by the use of impure waters are undesirable color, improper or lumpy size, and harshness in some of the finer papers. Aside from actual faults in the paper as finished, larger quantities of bleach and of alum (in applying the size) are consumed by impure water, thus increasing cost of manufacture. Impurities which seem inconsiderable, and would be so under other conditions, become important when the quantity of water here employed is taken into consideration. In this case the amount of sodium salts in the water is relatively unimportant so long as the objectionable metals are removed. The presence of organic matter in the water used by the paper mill is to be avoided in all cases, for no treatment short of distillation has been devised for removing this satisfactorily, and marked discoloration is caused in the paper produced by the use of water so contaminated.

Fabric Finishers, Bleachers, and Laundries—Here it is also necessary to have as pure water as it is possible to obtain. In the degumming of silk, particularly, the soap solutions must be prepared from water free from metals which produce insoluble compounds with the fatty acids of the soaps, as these attach themselves firmly to the fiber and make the finished silk harsh to the touch, and seriously affect its subsequent dyeing. Wool scouring and all operations involving the use of soap must take place in water free from salts of calcium, magnesium, and the heavy metals, if best results are to be obtained. In bleaching operations, it is also necessary that the water be as free as possible from organic matter—such as is frequently found in shallow wells—since such matter must of necessity be oxidized before the bleach can have the desired effect on the fiber. The boiling out of cotton is less likely to be affected by impurities in the water used, but even here it is necessary to have absolutely clear water and highly desirable that it be free from hardness on account of the effect dissolved salts may have on its subsequent dyeing.

Dyeing—In the dyehouse the faults of earlier mistreatment given the fabric are developed. Streaky dyeing is often the result of the presence of insoluble salts in the fabric or of the influence (either in resisting or mordanting the dye) of mineral salts left in the fabric from previous treatment. The water of the dye bath must be free from elements which would precipitate the dye. This condition is only to be satisfied in all cases by perfectly neutral water free from calcium, magnesium, or the heavy metals.

Chemicals—In strictly chemical operations, where water is used as a solvent from which to crystallize other substances, the purity of the product is essentially dependent on the purity of the water used. For this reason it is almost universal practice in the preparation of pure reagents and chemicals to use distilled water. In some cases it is possible to use natural waters which are practically free from dissolved solids, and in others softened water may be used, but in general the presence of even minute amounts of impurities is sufficient to disqualify a water for this use.

Steam Production—Steam production becomes actually dangerous where very hard waters or those containing large amounts of dissolved salts are used. The use of hard waters in boilers is not only an economic crime, but an actual danger to operators of steam plants. The formation of scale on the heating surfaces of boilers causes immediate reduction in the heat conductivity of those surfaces, resulting in unnecessary losses of fuel, and, if the scale becomes thick enough and cracks, may cause dangerous explosions. The presence of large amounts of dissolved solids, particularly the soda alkalies and organic matter, in boiler feed water is no less a source of danger from the fact that foaming and priming in the boiler are likely to result in exposing crown sheets and thus cause explosions. This danger is also less easy to overcome, and while many remedies have been proposed, few short of distillation have been found which will cure any but the mildest cases. Scale formation is less important in locomotive boilers than in stationary plants, since other causes, which do not affect stationary boilers, make necessary the complete cleaning out of locomotive boilers at short intervals. However, the extremely variable load on locomotives, which may change by several hundred per cent of itself in successive minutes, makes them particularly liable to foaming and priming. Boilers in ocean-going steamships are less liable to the difficulties of other boilers, because it is necessary to operate them in connection with efficient condensing systems which reduce the amount of raw water needed to a low minimum, and even the make-up water is distilled. Vessels on fresh water do not lend themselves to the use of water-treating plants, and consequently boiler compounds are often used in them where necessity may require it.

Condensers and Ice Making—Cooling water used for condensers need possess no other essential quality than low temperature, although excessively muddy water is to be avoided. Where water is frozen to ice, the quantity of dissolved solids becomes important. Aside from the lowering of the freezing point which comes from dissolved substances, the presence of excessive amounts of soluble impurities causes cloudy ice by being precipitated or crystallized from solution as the water freezes. Until quite recently it has been practice to distil all water used for this purpose, but the increasing commercial use of artificial ice, as distinct from its domestic use, and the development of efficient water-softening apparatus have made possible the use of treated water for this purpose. The absence of salts of calcium, magnesium, and the heavy metals is imperative and a reduction of the other dissolved substances to a minimum is necessary before undistilled water can be successfully used for ice manufacture.

Removal of Suspended Matter

Turbidity is removed from natural water by ordinary processes of filtration. The most usual type of equipment used for this purpose is the ordinary sand filter. Where plenty of space is available, gravity filters are used which consist of large beds of quartz sand through which the water is passed. Municipal water-treating plants are probably the best examples of this type of apparatus. Here the filter consists of a large, comparatively shallow tank containing a sand layer several feet in thickness and provided with strainers at the bottom through which the filtered water passes to storage. Gravity is depended upon to force the water through the filter. Bactericidal doses of chlorine are usually added to the water before filtration to reduce its bacterial content, and aluminium sulfate, with or without precipitating doses of alkali, is added to coagulate the suspended matter and increase the efficiency of the filtering operation. The sand filter beds become clogged in the course of time and are washed at convenient intervals by forking the sand while water is passed through. Pressure sand filters are frequently employed where space is limited. These consist essentially of a sand bed in a tank so arranged as to permit pressure to be applied to increase the rate of flow. In this type of filter the thickness of the layer of sand is proportionately greater than its area—just the reverse of the usual gravity filter. In this case washing is effected by forcing a flow of water back through the filter. Coke, charcoal, and other types of sand sometimes replace quartz sand entirely or in part, but the preferred material in most cases is pure quartz sand. The use of limestone or marble chips is sometimes convenient where water high in acidity is to be treated.

Removal of Dissolved Salts

Two methods of removal of objectionable dissolved salts are in common use, the lime-soda ash precipitation method and zeolite interchangers. Both depend for their efficiency on the formation of an insoluble salt of the objectionable metal and its replacement by sodium.

Precipitation Method—The precipitation method is carried out either hot or cold as the circumstances may indicate, and consists essentially in adding to the water precipitants for the calcium and magnesium salts and filtering off the precipitate before use. Lime, either quick or hydrated, soda ash, and sometimes trisodium phosphate are the reagents most frequently employed. Lime neutralizes any acidity in the water, especially carbonic acid, and precipitates calcium from bicarbonate, which it converts to the insoluble carbonate. For this purpose it is preferred to soda ash or other neutralizing agents because it actually reduces the amount of dissolved solids in the water by being itself precipitated. Magnesium is also precipitated as hydroxide by the lime treatment. Soda ash is used to precipitate calcium from salts other than bicarbonate by converting it to the insoluble carbonate. Sometimes part of the soda ash is replaced by trisodium phosphate, where the water treated is high in magnesium, to insure its complete removal. Other reagents have been employed in special cases, especially barium salts to remove sulfates, but in general precipitation plants use only soda ash and lime, which suffice for the treatment of the great majority of hard waters.

These precipitation reactions may be carried out either hot or cold. Ordinarily, the cold process is preferred in spite of the comparatively slow settling of precipitates. The hot process gains in the speed of precipitation, but the increased solubility of the precipitates in hot water is often a disadvantage. When preheaters are used, it is frequent practice to place these before the precipitating system in order to reduce the calcium bicarbonate hardness of the water before treatment. The ease with which calcium bicarbonate breaks down in hot water to carbon dioxide and calcium carbonate is thus utilized.

The equipment of a precipitation water softener consists of three essential pieces of apparatus, which may or may not be combined into a single unit: a reagent feeder, a reaction vessel in which the reagents are mixed with the raw water, and a means of separating the treated water from the precipitates. The difference between the hot and cold processes is that the former is carried out in a closed system and the latter in an open one.

The reagents are dissolved in a sufficient quantity of water and, in the case of continuous softeners, added by mechanical means in a fixed proportion to the raw water as it goes into the reaction vessel. In discontinuous systems this is not necessary, the solution of reagents being run into the raw water in the reaction vessel from a dissolving tank. If sufficient time be allowed in the discontinuous system for the precipitate to settle, it is often possible to do away with filters. Any type of filter may be used, but sand is preferred. Continuous processes have the obvious advantage, however, of requiring less space, and are generally more efficient from an investment point of view. In the continuous process, means are provided for feeding the reagents from pump or other device operated by the force of the raw water as it runs into the reaction chamber. A small turbine or water wheel is placed in a by-pass from the supply line and is so regulated as to drive a pump which supplies quantities of reagent solution directly proportional to the amount of raw water. While separate units for precipitating and settling may be used, it is common practice to build the reaction chamber as a vertical, open tube in the center of the settling tank. In this case the water mixed with the reagents is fed into the top of the reaction chamber, through which it flows downward to the bottom of the settling tank and upward in that to a filter built as an annular ring between the two at the top. The flow in the settling chamber must be sufficiently slow to permit of the settling of the precipitates in spite of it. The filter at the top is ordinarily operated by a slight head of water in the reaction chamber above the level of the filter overflow. The bottom of the tank (usually conical) is provided with means for removing precipitates periodically. The flow through the filter is also upward. It may be composed of any fibrous material which mats sufficiently to hold the precipitates, or it may even be sand. From the filter clear water passes to storage. The cubic capacity of continuous softeners should be sufficient to allow as complete settling as possible. Usually they are designed to hold four to six hours' supply of water.

ZEOLITE INTERCHANGERS—Essentially, zeolite softeners consist of filters of granular sodium aluminium silicate of such a character that the sodium ion is easily replaced by an alkaline earth metal. The alkaline earth compounds are insoluble and remain in the filter, but they can be reconverted to the sodium compounds by passing in an excess of sodium chloride solution. As installed, the equipment consists of one or more softening tanks in which the zeolite filters are placed and a supplementary tank for sodium chloride solution for the regeneration of the zeolite.

The operation of these plants is extremely simple and requires little attention. The raw water is passed continuously through the bed of zeolite until the effluent begins to show hardness by the soap test—i. e., until the sodium of the zeolite has been replaced by other metals. At this point the zeolite is cut out of the system and regenerated by passing sodium chloride solution through it. After the regeneration has been completed the excess of salt solution and the waste products formed are washed out of the mass, which is then ready to return to the system. This operation requires an hour or less for completion from the removal of the zeolite from the system until its return, since the whole thing is accomplished by means of the simple turning of valves controlling the flow of water and solution. Naturally, continuous operation can be had only by the use of two such softeners, but where relief periods are permissible, one will suffice.

The two methods are identical in principle, the difference being in the solubility of the compounds formed. In the precipitation treatment, complete removal of hardness is not possible on account of the slight solubility of the precipitated calcium carbonate in cold water. While its removal is virtually complete, it is impossible to reduce the hardness below one grain per gallon where calcium carbonate is in contact with the water, and in practice it is seldom possible to go below three grains per gallon consistently. In the case of zeolite softeners the limit reached in practice is so low that no hardness can be detected by soap solution. The precipitation method actually reduces the amount of dissolved salts, especially where a large part of the hardness is due to calcium bicarbonate, while the zeolite softeners simply exchange sodium for other ions without changing the ionic concentration. This latter may be a disadvantage where the water treated is very hard and is used for a boiler where foaming and priming may be of importance. Variation in the hardness of the water treated causes a corresponding inverse variation in the capacity of the zeolite equipment, but must be equalized by variations in the quantity of reagent added to precipitators without changing their capacity. Frequently it is practice to precede zeolite softeners by lime precipitators to remove the calcium bicarbonate hardness where this factor would greatly reduce their capacity otherwise. Their usefulness is greatest in treating water of medium or low hardness to produce extreme softness in the treated water, as in laundry operations. Any considerable amount of sodium salts in the raw water nullifies the action of the zeolite, and iron and manganese in the raw water form compounds with the zeolite which are not regenerated by sodium chloride solution. Otherwise, there are no particular limitations on their use. Precipitation softeners possess the advantage of having their capacities unaffected by variations in the hardness of the water treated, they reduce the ionic concentration of dissolved matter, and they are equally efficient in treating all waters. Their chief disadvantage consists in the necessity of close control to compensate for variations in the raw water and to guard against the addition of excesses of reagents which may be as objectionable as the constituents they are designed to remove.

TREATMENT OF BOILER WATER—In the case of boiler water a special type of treatment is frequently used which gives even better results in many instances than either of the foregoing methods and at less expense. This consists in introducing treatment directly into the boiler itself. In this way all equipment investments are eliminated and some of the treatments which can be applied in this way are more efficient than those used in other equipment. Treatment of electrolytic corrosion, which may result from the presence of appreciable quantities of soluble or hydrolyzable salts (magnesium chloride), by the addition of metallic zinc to the boiler itself has been very successful. Foaming can frequently be treated in this way which may be even aggravated by other treatments. This field, however, is a fertile one for quacks of various kinds, whose nostrums vary all the way from utterly innocuous mixtures to positively and dangerously harmful ones. Some few firms have given the subject careful thought, however, and have achieved remarkable results where other methods have failed. This subject is such a special case of water treatment that it cannot be given the full discussion it deserves here.

Mechanical Stokers and the Chemical Industries

By Walter H. Wood

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THE use of mechanical stokers as a means of supplying heat for the numerous and varied processes in the chemical industries has not as yet been given very serious consideration. There may possibly be several reasons for this.

First of all, competition among stoker manufacturers has been quite keen in the past, and the sales efforts have naturally been directed along the line which offers the least resistance. Since the use of stokers in steam generating plants has presented a favorable and fully developed field to the stoker manufacturer, it is hardly reasonable to suppose that a manufacturer would spend much time or effort in the development of a new and uncertain field in the face of existing competition.

Another reason why stokers have not found general application among the chemical industries lies in the fact that many of the chemical processes are more or less intermittent, requiring the application of heat at a definite rate for a certain period of time, followed by a period of no heat demand. In order that a stoker and its furnace may perform their functions with the best economy, the stoker should operate fairly uniformly and without frequent interruption. Otherwise, the fuel on the stoker will at one time be burning with an insufficient amount of air, resulting in loss due to the evolving of unburned combustible gases, and at another period of time there will be more air supplied to the fuel bed than is necessary for economical burning of the coal in order that the furnace temperature may be brought up to the desired point quickly. For this reason oil and gas find a more ready application in the chemical processes than do mechanical stokers. If it were possible to conceive of a stoker and furnace operating continuously and delivering the products of combustion of the fuel through channels to the different places where heat application is required, the stoker might find a pretty general use in chemical industries. It would, of course, be necessary to provide dampers for directing the heated gases through different channels and at the same time to regulate the amount of heat delivered at any given point, and it would also be necessary to have a sufficient number of places where the heat would be used to enable the stoker to be operated at a fairly constant rate and at the same time have the heat derived from the fuel used without undue waste. There might be times during such method of operating when the heat generated in the furnace would not be required in the various processes, and at such times the heat might be applied in heating water for use about the plant, or possibly as an auxiliary means of generating steam for use in engines and turbines. If such an application of stokers in the chemical industries is possible, it would, of course, involve the development of a load curve for a given process which would insure against unnecessary waste, and enable the stoker and furnace to operate at a point of maximum efficiency. Such an arrangement would result in good economy in the use of the fuel and might afford a means of reducing to some extent the labor about the plant.

Stoker application somewhat along this line has been made with very satisfactory results in some of the oil refineries. The stokers have been used for furnishing heat to oil stills, but no attempt has been made to direct the gases from a given furnace to any stills other than the one served by its stoker.

One large chemical industry has done a considerable amount of experimenting in the use of a stoker for obtaining the oxide of a metal from its ore by mixing the ore with anthracite fuel and burning the same on the stoker. There is not much information available, however, regarding this particular stoker application.

Efforts have been made to apply stokers for the production of carbon dioxide gas for use in certain industries. It appears that the analysis of such gas should show at least 16 per cent carbon dioxide content to make the application worth while. This field might become attractive, provided the carbon dioxide content can be maintained sufficiently high and all the gas from the fuel bed made use of, and at the same time insure against waste of the heat generated in the furnace when the fuel is burned.

In the operation of a forced draft chain grate stoker, especially when burning anthracite coal as a fuel, the gases rising from the fuel bed at the point where ignition takes place and for the first foot or two thereafter usually contain a very high percentage of carbon monoxide. It might be possible to so arrange a furnace equipped with such a type of stoker as to permit of withdrawal from the furnace of gases running high in carbon monoxide, which gases could be used as a reducing agent while the remainder of the gases in the furnace could be directed into the boiler for the purpose of generating steam.

There is one use of stokers in what might perhaps be termed a chemical industry, which has proved very successful. The great majority of the furnaces for heat treatment of steel in this country are equipped with stokers. This application has resulted in reducing quite materially the labor required about the furnace, at the same time giving a much more uniform product than can be obtained by hand firing.

STEAM GENERATION THE PRINCIPAL FIELD FOR MECHANICAL STOKERS

Any use to which the mechanical stoker may be put in the chemical industries for furnishing heat to any of the processes may not result in enlarging the field for the stoker manufacturer to any very considerable extent, but there is one very important application of mechanical stokers to almost every industry which uses steam—and that is in connection with boiler furnaces.

In the one hundred and fifty answers to a questionnaire recently sent to as many plants of chemical industries, approximately one-half of these plants reported that their furnaces were hand-fired. The total boiler-horse power installed in these hand-fired plants amounted to approximately 300,000 boiler-horse power. From this it is evident that in the chemical industries at large there must be a vast number of steam generating plants which are being fired by hand, many of which no doubt are of sufficient size to make the use of stokers well worth while. Up to the present time far too little thought has been given by the management of such industries concerning their power plants. In many of the industries, such as paper mills, where much steam is needed, the power plant has in the past been thought of only as a necessary evil, and little consideration has been given to it by the management except at times when for some reason the power plant fails to perform its function and as a result the production of the mill is stopped. Usually at such times the management is none too complimentary in the remarks or criticisms of the power plant and the men operating the same. These power plants are, as a matter of fact, the heart of the industry, for when the power plant is forced to shut down the rest of the plant is about ready to do the same. The management of any industry should realize that the power plant in that industry is one of its several important departments, which should be given just as much consideration as to its design, equipment, and operation as any other department in that industry. Such a position is the only sane one for a management to take, because when the power plant as a department of the industry is properly designed and equipped and properly operated, it does its share along with the other departments in turning out a product at the lowest possible cost.

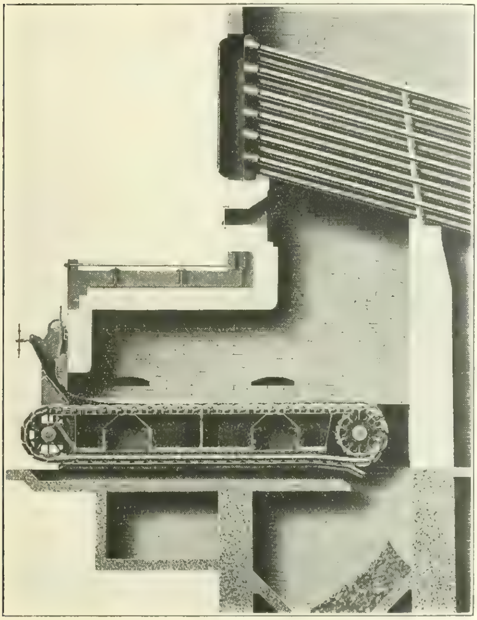

Fig. 1

In selecting stokers for use in any industry, whether that stoker is to be used for steam generation or in connection with some special process, there are several points which should be given careful consideration. Chief among these may be mentioned the selection of a stoker best suited to burn the coal which is available at the plant in question. In case more than one variety of fuel is available, a stoker should be selected which will give the lowest steam production costs when the prices of the coals are taken into consideration. In many instances the plants are so located that both anthracite and bituminous fuels can be had at reasonable prices, and where this is the case it is well to consider the use of the stoker which will burn one of the fuels economically and which will be able to make use of the other fuel with at least a fair degree of success in the event that the regular fuel supply should be interrupted on account of strikes and other conditions, or if the price differential between these varieties of fuels varies enough to warrant changing from one fuel to another.

Geographical Location of Plants and Fuels Available

Different sections of the country are naturally supplied with different kinds of fuels, and usually there is one type of stoker best suited for burning a given fuel. For example, the anthracite coals are burned far more economically on the forced draft chain grate than on any other type of firing machine, and with this machine the highest possible rates of combustion of that fuel are obtainable. The reasons for this lie in the facts that anthracite coal must not be agitated mechanically or disturbed while it is burning, and it should be burned in thin and very even fuel beds. The chain grate stoker is practically the only type of stoker that fulfils these conditions.

The natural draft chain grate does not answer the requirements of an anthracite stoker, because when the anthracite fuel bed is once ignited, the fuel should be burned as rapidly as possible, and this condition can be accomplished only by supplying air for combustion to the fuel bed from beneath the same, at the same time maintaining practically atmospheric pressure in the furnace above the fuel bed. This can be done with the forced draft chain grate, but not with a natural draft chain grate for in order to get the necessary air through the fuel bed on a natural draft stoker, the pressure in the furnace would be so far below atmospheric that ignition of the fuel would be quite impossible to maintain. Practically, no better results can be had with anthracite fuel on any stoker, other than the forced draft chain grate, than can be secured by hand firing on a suitable grate with an ash-pit blast. The chemical industries in sections of the country where anthracite coal can be had at reasonable prices, should, therefore, give due consideration to this type of stoker. These territories include Eastern Pennsylvania, New Jersey, New York, the New England States, and parts of Canada. It might be said here that the forced draft chain grate stoker has in the past four years become quite a favorite stoker for use with the bituminous fuels which do not coke to any great degree, or which, if they do so, form a coke which is soft and friable enough while it is burning to break down of its own weight. Such fuels burn out quite completely on this type of stoker. But there are certain fuels of the bituminous variety, especially those semibituminous coals from the Clearfield and

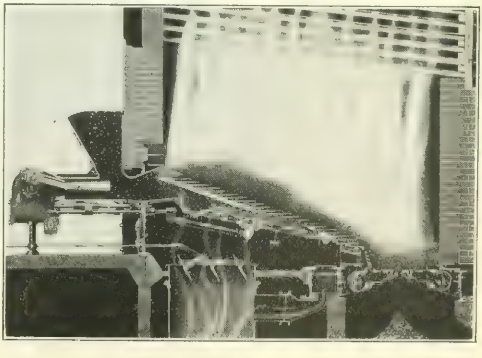

Fig. 2

Cumberland regions—in fact, most Pennsylvania semibituminous coals lying east of the Pittsburgh seam—which are not burned without excessive ash-pit losses, owing to the nature of the coke formed. Coke breeze makes as satisfactory fuel for the forced draft chain grate as does the anthracite coal. The extensive graphitic anthracite deposits in Rhode Island will probably be developed at an early date as a source of fuel, experiments being under way at the present time in using this fuel on forced draft chain grate stokers, and in pulverized fuel furnaces. Such a development will be of great benefit to the industries of New England especially. A typical forced draft traveling grate stoker is shown in Fig. 1.

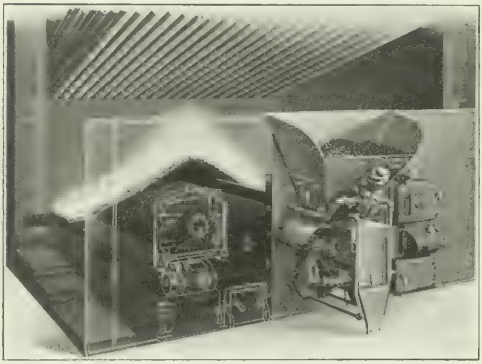

Fig. 3

The semibituminous fuels mined in Pennsylvania to the east of the Pittsburgh district in the Connellsville section, and in Cambria, Clearfield, and Indiana Counties, as well as the New River and Pocahontas and Cumberland coals from West Virginia and Maryland, are burned to the best advantage on the multiple retort stokers. While this type of stoker (Fig. 2) is particularly well suited to the semibituminous fuel, it is used quite extensively for burning the better grades of bituminous. The semibituminous coals as a rule are low in ash content with volatile matter ranging between 16 and 26 or 28 per cent, and usually show a higher temperature of fusion of the clinker in the ash than do any other coals; therefore, high combustion rates are obtainable with this kind of coal, and at the same time little difficulty is experienced in cleaning fires. This variety of coal is used principally east of Pittsburgh and in the New England States. The low ash content of most of the coals of this kind makes their shipment on the long hauls to New England and elsewhere more economical than the shipment of low heat value, high ash fuels.

The bituminous coals are quite widely distributed in groups over the country, being found principally in Alabama, West Virginia, Pennsylvania and Ohio, in Illinois and Indiana, Kansas, Oklahoma and Iowa, in Texas and Arkansas, and in Colorado and New Mexico. The generally accepted reason for classing the fuels from these different groups as bituminous coals, is that their volatile combustible content ranges between the semibituminous and the sub-bituminous fuels, or from, say, 28 to 35 or 40 per cent. The bituminous coals often contain more ash than the semibituminous coals, and as a class they have a somewhat lower heat value and a lower fusing temperature of the clinker in the ash. Owing to the greater amount of ash in bituminous coals and to the lower fusibility of the same, the multiple retort type of stoker sometimes has difficulty in handling these coals successfully. This type of stoker has a dump grate running the full width of the furnace, and in some installations, because of narrow aisles, etc., it is impossible to get a chance to dislodge clinkers from the bridge walls, which may adhere to the same. For this reason fuels of this kind are very often handled with greatest success on the underfeed type of stoker, such as illustrated in Fig. 3. In most underfeed stokers the ash can be dumped at the sides of the furnaces, and if clinkers adhere to the brickwork, this occurs along the side walls where the clinkers can easily be dislodged and removed. The underfeed stoker is generally a forced draft stoker, and high capacities and efficiencies are obtainable with it when burning bituminous coals. The natural draft chain grate stoker (Fig. 4) has also been used quite extensively in burning bituminous coals, especially those having very low fusing temperatures of clinker in the ash, such as the Illinois, Ohio, Iowa, and Kansas coals. It might be said here that the forced draft chain grate stoker is used quite extensively now as a firing machine for these fuels, and very high rating and efficiencies are being obtained in some of the most important plants in the Middle West with this stoker.

The sub-bituminous coals of Wyoming, Montana and other of the western states can be burned with only a fair degree of success with most stokers, except with the forced draft chain grate stoker, which is showing remarkably high ratings and efficiencies with these fuels. The low temperature at which the clinker fuses, running often as low as 1800° F., does not interfere with the results either as to efficiency or capacity.

Lignite has not as yet become one of the principal fuels of the country, although there are very extensive deposits of this fuel, especially in Texas and North Dakota. In the one state, oil is too strong a competitor as a fuel, and in the other, industries are not developed to such an extent as to require large power plants. The forced draft chain grate stoker burns lignite, with perhaps as good results as can be obtained with any of the other stokers, and it will in time probably be the principal stoker for this kind of fuel.

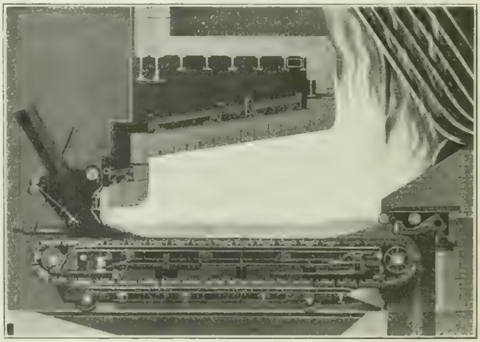

Fig. 4

In concluding, it might be added that the pulverized fuel furnace is now developed to such a degree that it can be used with practically any coal mined, and the capacities and efficiencies obtainable with these furnaces are higher than those which can be secured with any stoker. It may not be impossible that this method of burning coal will find application in many of the chemical industries, as a means of supplying heat for all kinds of process work.

Electrical Motors for Industrial Service

By J. L. McK. Yardley

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IT IS in the nature of a major accomplishment that the multitudinous industrial operations requiring power may practically all be supplied through proper applications of electrical motors. Not only this, but it is a fact that very considerable standardization has been achieved, and that the gamut of applications is economically covered by a number of types and sizes of motors which is comparatively insignificant. Perceiving the chaos which would result from unguided development and react upon industrial progress, comprehensive classes with logical characteristics and ratings have been determined upon as those to be generally manufactured, from which intelligent selection may be made for the particular application involved. Preference for alternating current over direct current has become well nigh universal, and 50 and 60 cycles are with increasing rapidity becoming the predominating frequencies.

The present satisfactory situation has come about in a natural and logical way as a result of a number of definite facts, chief among which, perhaps, is that 50 or 60-cycle power is the cheapest and most economical power to generate, transmit, and distribute, which is at the same time very economical and flexible to apply in diverse industrial operations. All important industries, with the exception of the electrochemical and electrometallurgical industries, are able to use alternating current in by far the major part of their power-consuming applications, and the electrochemical and electrometallurgical industries use alternating current motors in preference to direct current wherever possible, owing to there being less surface of copper exposed to chemical action. Here and there an industrial plant or a whole corporation such as the Ford Motor Company has settled upon direct current owing to its extreme flexibility, and uses nothing but direct current motors. These are usually cases where the power is generated as direct current within the plant and there are no extra transmission or conversion losses. There are, moreover, a number of power applications, some occurring in nearly every industrial plant, for which direct current is essential or generally far preferable. Those which may be mentioned include fans and blowers, elevators, cranes, rubber calenders, paper driers and calenders, reversing rolling mills, adjustable speed mills, such as cold rolls, larry cars, industrial and mining locomotives, and electrolytic cells. Applications for which direct current is legitimately preferable or necessary are those in which great speed range, or great starting torque, or frequent reversal is required. Accordingly, practically every industrial plant requires or employs at least a small amount of direct current equipment whether or not the major part is for alternating current.

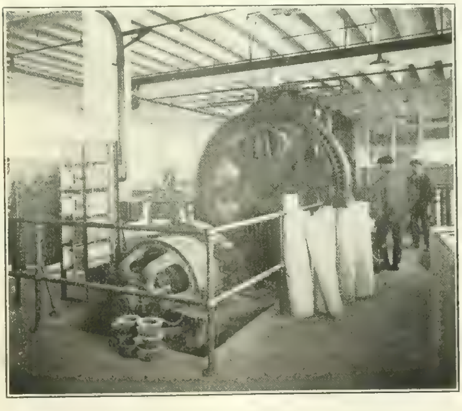


Fig. 1—Complete Rubber Calender Installation

Since this application usually requires capability of adjustment through a 4 to 1 speed range—that is, say, from 283 to 1130 r. p. m. for a 50 h. p. application to from 175 or 200 to 700 or 800 r. p. m. for a 250 or 200 h. p. application, direct current is found more suitable than alternating current; and, in the larger applications, operation from double voltage circuits is found more suitable, in order to reduce expense in equipment and somewhat better speed regulation with varying loads. The 3-wire, 115–230-volt circuit for this purpose is usually provided by a 250-volt industrial type synchronous converter.

Motors are rated at 50° C. on a constant torque basis.

Sixty-cycle power can be generated at the lowest first cost. The ordinary inter-works distribution, or short distance transmission, of 50 or 60-cycle power is as cheap and economical as for 25-cycle power except when very heavy currents—2500 amperes and above—are to be carried in one circuit. It has a flexibility as to permissible normal motor speeds which is sufficient for the great majority of industrial plant applications, and is obviously far superior to 25 cycles. In addition, the higher frequency motor for a given horse power and speed is considerably cheaper. Twenty-five cycle power has advantages in applications where the fundamental speed is low. The following normal speeds (approximately) are obtainable depending upon the number of poles.

Poles	25 Cycles R. p. M.	50 Cycles R. p. M.	60 Cycles R. p. M.	Motors Obtainable for 60 Cycles Horse Power
2	1440 to 1500	2880 to 3000	3450 to 3600	$^1/_2$ to 50
4	720 to 750	1440 to 1500	1720 to 1800	$^1/_4$ to 350
6	480 to 500	960 to 1000	1150 to 1200	$^1/_2$ to 500
8	360 to 375	720 to 750	865 to 900	$^1/_2$ to 1750
10	288 to 300	576 to 600	690 to 720	$7^1/_2$ to ...
12	240 to 250	480 to 500	576 to 600	$7^1/_2$ to ...
14	205 to 214	410 to 428	493 to 514	
16	... to 187.5	360 to 375	432 to 450	
18	... to ...	... to ...	385 to 400	
20	... to .	... to ...	345 to 360	

In this article the discussion of electrical motors for industrial service will be confined to the 60-cycle, 3-phase motor, at standard voltages of 220, 440, and 550 volts. For other motors the same general principles apply. Large alternating current motors in all industries are usually at 440, 550, or 2200 volts, or may even be at higher voltage. The textile industry, employing vast quantities of small 550-volt motors, may be cited as perhaps the most conspicuous example of the application of relatively high voltage in small motors. It is also the principal exception to the very general adoption of either 440 or 220 volts for industrial motors for general purposes.

Temperature Rating

In order that industry may secure the benefits of uniformity and standardization in motor manufacture, it has become "recommended prac-

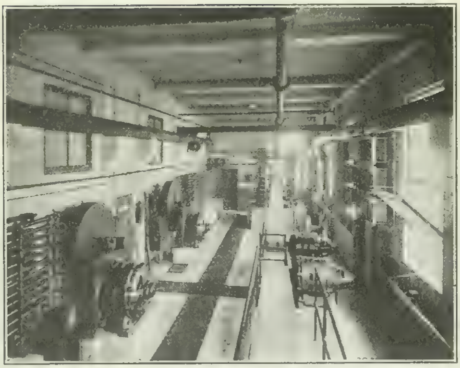


FIG. 2—TWO 75-H. P., TYPE "CS" MOTORS TO THE LEFT, GEARED TO LINE SHAFTS FROM WHICH ARE DRIVEN VARIOUS MACHINES. TO THE RIGHT ARE TWO 50-H. P., TYPE "CW" MOTORS BELTED TO AMMONIA COMPRESSORS IN THE SAME ROOM

tice" that an open type, general purpose motor shall be capable of carrying full rated load continuously with a temperature rise not exceeding 40° C., and that it shall be so designed as to be capable of carrying sustained overload (in no event exceeding 50 per cent overload) within a temperature of 90° C. measured by thermometer. Many special application motors, and particularly synchronous motors and large induction motors, will be manufactured in accordance with generally accepted practice for such apparatus so as to be capable of carrying full rated load continuously with a temperature rise not exceeding 50° C., and will not be so designed as to be capable of carrying sustained overloads appreciably above full rated load without exceeding desirable temperature. This method of rating is a common sense method, being based upon the fact that insulation of the type universally employed in industrial motors begins to deteriorate if operated at temperatures above 105° C., and that it has been found in practice that a differential, called "conventional allowance" by A. I. E. E. standards, of 15° C. is likely to exist between the temperature of some point at the surface of the conductor and the highest obtainable thermometer measurement. Furthermore, it pays to analyze power requirements more thoroughly in installing a large motor than a small one, so as not to have excess capacity which will never be used. Power requirements are likely to vary more from day to day with a small general purpose motor than with a large motor. This makes sustained capacity in excess of normal rating more essential in the general purpose motor. Hence, the logical outcome has been to rate general purpose motors at 40° C., with some greater inherent overload capacity than the larger and special motors which are rated at 50° C.

ADVANTAGES OF MOTOR DRIVE

While the advantages of driving mechanical applications by electrical motors are so universally recognized that with hardly an exception all new industrial construction is completely electrified at the outset, there are very many old mills or factories now completely equipped with steam drive which, when the necessity for renewal, extension, or increased production in the same space arises, must view electrification with utmost practicality and adopt it only if analysis indicates that tangible benefits from electrical drive will warrant writing off corresponding items in the plant account, representing capital already expended. It is a fact that analysis shows electrical drive to be truly economical in most of such cases, even when process steam in considerable quantity is required.

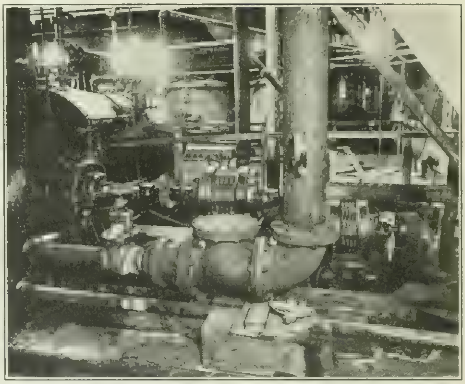


FIG. 3—15-H. P., TYPE "CS" MOTOR TO THE LEFT, DIRECTLY CONNECTED TO WATER CIRCULATING PUMP, AND 5-H. P. "CS" MOTOR TO THE RIGHT, BELTED TO PREHEATER PUMP IN A CHLORINE AND CAUSTIC SODA PLANT

Motor drive eliminates the complicated system of line shafts, belts, clutches, and pulleys. This system, necessary with steam drive, is awkward to instal and expensive to maintain; it requires constant attention to keep it in working order; it wastes a large amount of power through friction; and it makes difficult the protection of operators against unnecessary risks of injury. With motor drive, each machine may have its own motor, forming a compact unit that can easily be safeguarded. Production is increased by motor drive because each machine can be maintained at its proper speed. The time lost on account of shutdown is materially reduced, as trouble with line shafts and belts is practically eliminated. Furthermore, as a majority of machines have individual motor drive, the operation as a whole is usually not materially affected by the shutting down of any one machine. A motor-driven plant is thoroughly flexible, since machines can be arranged in any desired location, according to the needs of production, and additions can be made conveniently and readily, so as to conform with the original layout. With engine drive, suitable location and arrangement of the line shafts largely govern the mill or factory layout and often place undesirable limits on it, especially where extensions are to be considered.

Electric power, being readily transmitted long distances to widely separated buildings and process operations, may be generated at a point removed from the dust of plant and located convenient to condensing water and fuel supply. Power charges can be accurately assigned to each department, thus improving the cost system and encouraging increased efficiency. With individual motor drive an ammeter can be used with each machine. This meter shows the current taken by the motor, and since the current consumption is constant or varies over a normal range under proper operation, irregular meter readings indicate at once that something is wrong and the fault in the operating conditions should be corrected. In this way trouble which might otherwise become serious before discovered can often be avoided. In addition, the current consumption will vary with the adjustment of the operating part of the machinery being driven, so that the meter provides an accurate indication as to the character of these adjustments and thus greatly aids in the production of the desired quality of material.

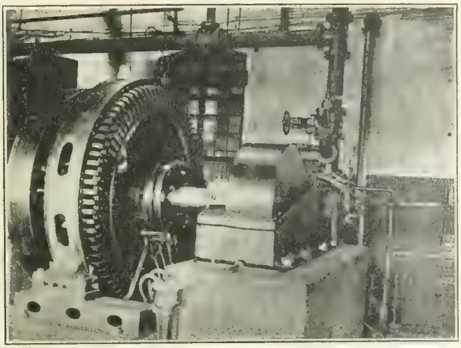


FIG. 4—ENGINE TYPE SYNCHRONOUS MOTOR DRIVING AIR COMPRESSOR. MOTOR LOCATED BEYOND DANGER FROM CORROSIVE FUMES OF CHEMICAL PLANTS

Electrification includes the advantages offered by the use of central station power. In most cases the cost of purchased power is less than the cost of power generated in a private plant, when all the factors of expense are taken into consideration, and, furthermore, the incidental advantages are of much value. The use of power purchased from a central station results in a much lower first cost of plant, while extensions can be readily made and the time and attention devoted to supervision of the power plant can all be given directly to production.

Electrification of existing mills and factories and the substitution of electrical motor drive for steam drive is probably held back more by insufficient capital than by any other cause. The supply of capital is, of course, limited. Old mills wear out in time. Many are difficult to modify economically. Executives often see better labor conditions developing in a new locality. So long as the old mill is able to continue in operation at a profit, despite its inefficiencies, better business judgment often decides that available capital can be more profitably invested in an entirely new property than in rejuvenating an old one.

In connection with this whole matter, it is well to appreciate the progress which has been made in the electrical motor itself since the day when it was still general practice to build steam-driven plants. It should be realized that this progress has been much greater than the corresponding progress in steam drive, so that any decisions made years ago may not be considered final as between systems nor detrimental to universal installation of electric motor drives. This progress is well illustrated by the following tabulation for the 10 h. p. induction motor:

H. P.	Poles	Type	Year	Price	Weight Lbs.	Efficiency %	Bearings In.
10	6	C	1902	$350 (equivalent to $1000 in May, 1922)	1100	83.5	$1^{3}/_{4} \times 4^{5}/_{8}$
10	6	CS	May, 1922	$234	270	88.5	$1^{3}/_{4} \times 4^{3}/_{4}$

In May, 1922, prices on 60-cycle, squirrel-cage motors were only 18 per cent above 1914 prices, although labor was 80 per cent higher and many materials were more costly. With weight and comparative cost reduced to a fraction and efficiency increased very appreciably in the past twenty years, the electric motor itself has become much more attractive economically; and since its reliability has also become established, it is the chief consideration in electrification.

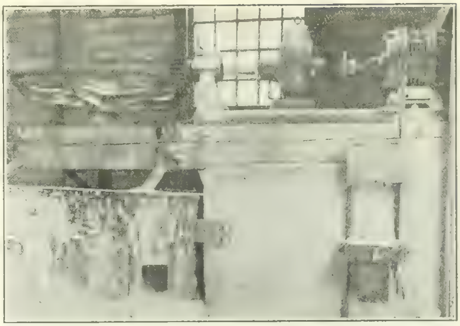


FIG. 5—7.5-H. P., 440 VOLT 3-PHASE, 60 CYCLE MOTOR DRIVING POTASH DRIER. THE SPEED OF MOTOR, 685 R. P. M., IS CHANGED THROUGH REDUCTION GEAR TO 50 R. P. M. CONTROL SWITCH IS MOUNTED ON CONCRETE WALL BELOW

MECHANICAL TYPES AND KINDS OF DRIVE

While, from an electrical point of view, the motor has been susceptible to standardization, producing a uniformity which tends towards economy in manufacture and in the supply of power to it, from a mechanical point of view the same thing has not been possible, owing to the diversity in the mechanical operations in industrial plants, for which power must be supplied. Accordingly, we have direct-coupled, flexibly coupled, geared, chain-driven, belted, back-geared, vertical motors, etc. With regard to methods of drive, the fundamental factors determining which should be employed are practically the same in all industries. Briefly, group or gang drive is seldom economically justified, except in cases where the group or gang consists of a comparatively large number of intermittently used, small-powered applications, all located near together, so that the driving motor may be considerably smaller than the total connected load, and the amount of shafting continuously running is not excessive. The small, general purpose machine shop is perhaps the most familiar and best illustration of this.

These usual mechanical types in general purpose industrial motors will be discussed in particular reference to some applications which, for mechanical or chemical reasons, exceed the suitability of general mechanical types, and require something special in the electrical design, either of the motor or of the control system. The rubber calender drive already referred to, and shown by Fig. 1, is one of those requiring special control.

ELECTRICAL MOTORS FOR CHEMICAL PLANTS

The smaller mechanical power applications in chemical plants of all kinds frequently require something special in the motor itself, in regard to its insulation. The following substances, frequently found in the atmosphere in mills, factories, and industrial plants of all kinds, and particularly chemical, electrochemical, and electrometallurgical plants where the substances are manufactured or used in quantity, are injurious to insulation:

(1) Oil—splashing, dripping, or flooding.
(2) Severe moisture conditions, dripping water, steam, high humidity.
(3) Carbon, iron, graphite, coal, coke, and abrasive dusts.
(4) Nitric, hydrochloric, sulfuric acid; ammonia; caustic soda or potash, alkali fumes.

In chemical plants or by-product coke plants, where the acid conditions are found to be so severe that a considerable amount of acid will condense and collect on the commutator, it is not advisable to use direct current motors, as the acid will attack the commutator and interfere with successful operation. The critical applications, as indicated, are usually the small ones. Large motors, where required by a large machine, or economically preferable in a group drive, are usually protected to a degree by greater distance from the injurious substance, by being placed in a separate room (Fig. 2) or by being specially ventilated with pure air. Where acid or alkali fumes are densest, the less driving mechanism to be attacked the better, and hence the more direct the drive the better. In some applications, therefore, it is practically essential that the motor be directly connected to, or very near, the source of dangerous fume, and it is not economical to give it special ventilation. These applications practically all come within the capacity of a 5, 7.5 or 10-h. p. motor, or thereabouts, and it is essential that motors thus applied have special protective insulation. These motors, and in fact all motors so far as possible employed in the four classes of service indicated above, should have squirrel-cage rotors, for the reason that such rotors can be readily dipped in a protective acid-resisting varnish, whereas slip rings, necessarily exposed, are ever subject to attack.

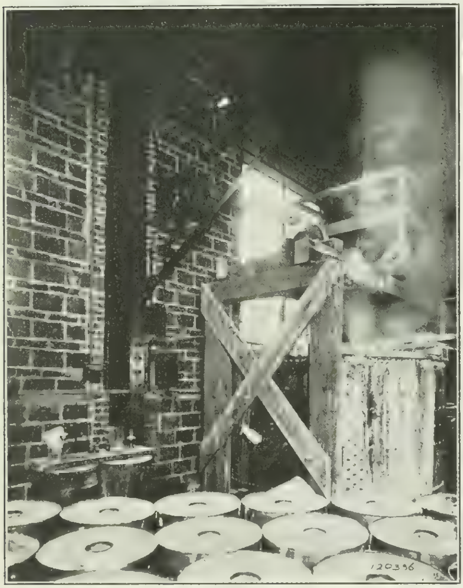


Fig. 6—5-H. P., Type "CS" Motor Mounted on Wall, and Belted to an Agitator in a Caustic Shed. Note Fumes from Agitator

The insulation employed on general purpose industrial motors is cotton fibrous material, impregnated with a substance having good insulation properties, which replaces the air between the fibers, even if it does not completely fill the spaces between the insulated conductors, entirely covers the fibers, renders them adherent to each other and to the conductor, does not produce interstices within itself as a consequence of evaporation of the solvent or through any other cause, does not flow during the operation of the machine at full working load at the temperature limit specified, and does not deteriorate under prolonged action of heat. The impregnation is an insulating varnish of linseed oil or asphaltum base, which, when baked at proper temperature, hardens while it retains some elasticity, or at least does not become brittle. The constituents of this varnish can be varied so as to produce a product little affected by any of the destructive materials which have been mentioned. The cotton fibrous material impregnated in the winding of the general industrial motor is, however, quickly and decidedly affected unless more perfectly coated with protective varnish. Moreover, under any of such conditions, an insulation of higher dielectric strength than the ordinary is desirable. Accordingly, a mica and fish paper wrapper is substituted for the treated cloth wrapper immediately adjacent to the conductors, and additional dippings of impregnating and coating varnish are supplied so as not to leave any little threads of fiber extending through the coating and exposed to oil, water, abrasive, or especially chemical action. When this is done, the motor winding is found to have a relatively long life.

This is usually accomplished by giving an increased number of dippings of thinner varnish and bakings, such as experience indicates is necessary to produce absolute impregnation, sealing, and a perfect covering which is hard and yet somewhat elastic. These extra dippings and bakings may be given wholly or in part to the coils alone in the case of open slot motors, or they must be given to the entire stator in the case of the partially closed slot motor. In the former case, coil replacements can be made in the field, while in the latter case, coil and end connections have the same dips and bakes as the rest of the stator. Some industrial plants have a practice for further protecting motor windings under such conditions, which consists of plastering the ends and vents with a mixture of asbestos, plaster of Paris, and shellac. No repairs are made on such motors, but where necessary they are rewound completely. Usually, however, dippings and bakings of coils and motor, if properly and thoroughly done, give all the protection that is necessary, and are economical. A balance must be struck between the cost and reliability of repairs with such treatment as can be given on the field and that of completely rewinding.

A practice which is worthy of recommendation as giving motors exposed to these conditions all the protection economically justified or desirable, follows a schedule of treatment in manufacture approximately as follows:

The usual standard motor of open slot construction, up to 25 or 50 h. p. at 600 volts, being treated as follows:

Uninsulated coil given at least one dip in asphaltum base varnish.

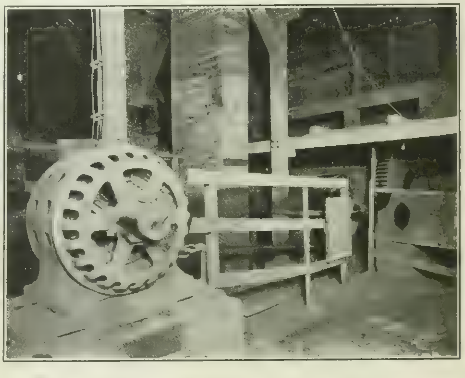


Fig. 7—Squirrel Cage Motor Belted to Grinder in Fertilizer Plant

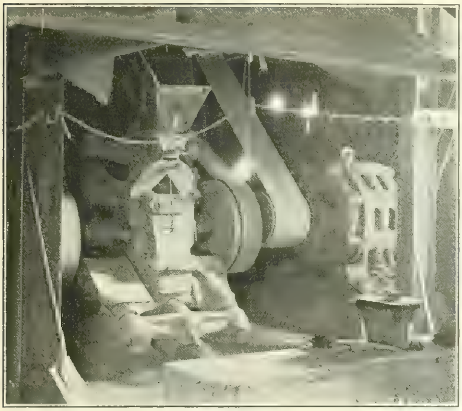


Fig. 8—100-H. P., 440 Volt, 3 Phase, 60-Cycle Mill Motor Belted to a Kent Mill Used for Crushing Bauxite. This Motor Also Drives a Conveyor

Treated cloth wrapper used.

Insulated coils give not less than one dip in linseed oil base varnish, or the partially closed slot construction with untaped end windings being given two or more dips in asphaltum base varnish, the special conditions mentioned above would be met as follows:

1—Open slot, at least two dips linseed oil base varnish on uninsulated coil, fish paper and mica wrapper not less than two dips same varnish on insulated coil.

Partially closed slot, end windings all taped, at least one dip asphaltum base varnish, followed by at least one dip linseed oil base varnish.

2—Open slot, same as No. 1.

Partially closed slot, same as No. 1, except all dips in asphaltum base varnish.

3—Open slot—recommended construction—at least two dips linseed oil base on uninsulated coil, mica wrapper, at least four dips same varnish on insulated coil, at least four dips on whole stator.

When partially closed slot motors are employed in this service at least four dips asphaltum base varnish for the completely wound stator are recommended.

The special purpose to be accomplished by all this dipping and baking is to procure a smooth, glossy surface with no breaks or rough spots for abrasive dusts to act upon, and to give increased dielectric strength, owing to materials of class No. 3 being such good conductors. Linseed oil is hard to dry where not exposed to air, and when not perfectly dry its insulating capacity is reduced. Asphaltum base varnish is a good insulator whether hard or not.

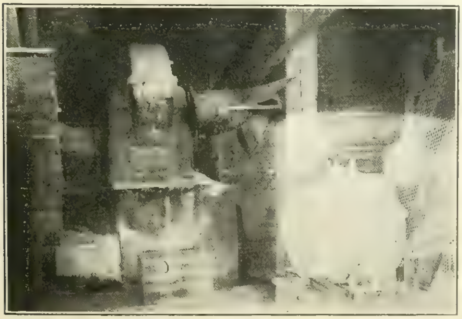


Fig. 9—30-H. P. Motor Driving Blower and Conveyor for Handling Alumina Tailings. Note Cloud of Alumina Dust in Which the Motor Operates, and the Degree to Which Dust Has Become Plastered over the Motor

4—Open slot—recommended construction—complete perfect coating essential, no fibers protruding; varnish, largely plastic asphalt with some linseed oil and gum—not less than two dips on uninsulated coil, mica wrapper, not less than four dips on insulated coil, not less than six dips on completely wound stator. This varnish has good filling qualities and good dielectric strength. It produces a fairly hard coating of sufficient elasticity and unaffected by these atmospheric impurities. It bakes in 8 hours at 110° C.

Where partially closed slot motors are employed in this service, a total of at least six dips in the same varnish for the completely wound stator are recommended.

Chemical Plant Applications

Liquor Handling.

(A) Lifting:

  (1) Direct-coupled, high-speed, motor-driven, centrifugal pumps (such as Fig. 3)—vertical units being especially desirable for protection of motor.

  (2) Smaller plunger pumps may be included in group drive along with small vacuum pumps, and also agitating or stirring mechanism. In such case motors are protected somewhat by distance.

  (3) Compressed air for corrosive liquors supplied by electrically driven compressor plant at distance from danger (Fig. 4).

(B) Agitation or stirring:

Whether in open tubs or vessels or in closed pots, autoclaves, etc., the power requirements of individual devices are small, about 1 to 2.5 h. p. The low-speed paddles or blades, or pump-like impellers are usually most satisfactorily driven by bevel gears from a cross shaft supported on the structure of the vessel, and finally belted through fast and loose pulleys to a common countershaft running at from 120 to 160 r. p. m., serving a number of vessels, as well as liquor pumps of plunger type, crushers and elevating devices for handling solids, and possibly vacuum pumps of small size in conjunction with individual closed vessels, or adjacent ovens for dehydrating or drying some of the products, and driven by constant speed, single reduction, belted motor. Fig. 5 shows similar device direct-motor driven through reduction gear, and Fig. 6 shows another operated by belted drive.

Solids Handling.

(A) Grinding and mixing:

  (1) Individual drive, direct coupled and flexibly coupled.

  (2) Belt drive (Fig. 7).

  (3) Slow-speed devices, usually by reduction gearing or countershafts. These devices usually take not over 5 or 6 h. p. each, except at starting, and are generally suitable for group drive.

(B) Crushing:

Individual drive by belt or gear, usually with suitable flywheel (Fig. 8).

(C) Conveying, mixing, screening (Fig. 9).

  (1) Mixing:

    (a) Worm and stirrer types are often in sizes suitable for individual drive, usually through gear trains.

    (b) Cylinder and ball mills, usually group drive.

  (2) Screening, small aggregate power:

    (a) Individual drive, on account of room taken up.

    (b) Included as a unit with the grinding equipment and driven by same motor.

Separating Materials.

(A) Solids: Screening, covered by "Solids Handling C2" above.

(B) Liquors:

  (1) Settling tanks, requiring pumps merely to fill and empty.

  (2) Centrifugals:

    (a) Geared up from usual standard motor.

    (b) Driven by special high-speed motor.

    Motor requires No. 4 special impregnation if liquor is corrosive.

Elevators and Hoists. As has been indicated, these are usually driven by direct current motors. In any case, total enclosing of control gear is required, or special ventilation for it, and special pipe ventilation, or special insulation for the motor. Both control and motor may, however, be installed in a separate chamber, and not in the usual space directly above the elevator shaft. These precautions must be considered since the elevator shaft acts as an excellent chimney and draws through it vapors released below.

Plauson Colloid Mill

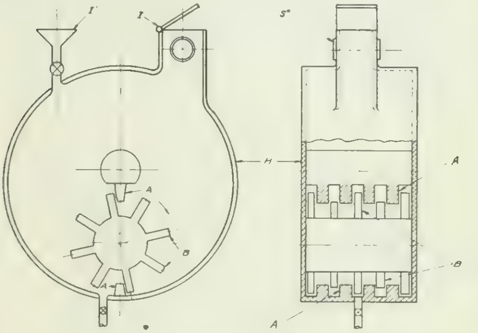
By W. J. Kelly

The Goodyear Tire & Rubber Co., Akron, Ohio

During the past two or three years considerable interest has been aroused in this country and Europe in the Plauson colloid mill. Several articles have appeared in the literature giving descriptions of the mill itself and speculations as to what might be expected of it, as well as some experimental data on products obtained from it. Practically nothing has been written on the power-consumption capacity or efficiency of the mill, and up to the present time very little is known on these phases of the operation of the machine. The attempt will be made in this article to clear up some of these points.

Description of the Mill

The Plauson mill is what might be called a beater mill. Referring to the sketch, the beaters are shown at *B* and the baffles or anvils, as Plauson prefers to call them, at *A*. *H* is the housing, *I*, *I'* are inlets or charging ports, and *O* is the outlet. *S* is a sight glass. The front and back of the housing are jacketed so that the mill may be either cooled or heated as occasion may require. The beaters revolve at high speed, and in the case of the turbine-driven mill attain 12,000–14,000 r. p. m., giving a peripheral speed of about 37,000 to 44,000 feet per minute.



Action of the Mill

Three theories have been advanced for the action of the mill. The first is that the blow delivered between the anvils and the beaters on the film of liquid is transmitted to all the particles in the suspension in that part of the mill, and if the force of the blow is great enough the particle is shattered. The second theory is that a shearing action takes place as the beaters pass between the anvils. The velocity gradient here is very high—viz., from zero on the anvil to the speed of the beater—and the clearance is only about 1 mm., hence, a big shearing action is possible. The third theory is less plausible than the others, and in this one it is assumed that at the instant of impact there is an instantaneous superheating of the liquid causing more or less of an explosion in the particle when the pressure is removed. This theory is based on the fact that the temperature of any liquid beaten in the mill rises very rapidly and water may be boiled in a few minutes.

Operation

As the mill is used at present for grinding solid materials, it is an intermittent machine. The charge usually consists of about 1 kg. of solid and 4 liters of liquid, and the mixture is subjected to the action of the beaters for about 10 minutes, after which the charge is removed through the outlet *O* and a new one put in. This operation can be modified by circulating a large batch, but the results are not usually so good as when the single small charge is employed, since there is no way of being sure that the whole of the batch as it is being circulated passes between the beaters and the anvils.

For use as an emulsifier the 3000-r. p. m. mill is being used successfully, and for this type of work it can be made to work continuously up to the capacity of the feeding and receiving tanks. It has a capacity of about 1.5 to 1.7 tons of water per hour when used in this manner. Better results are obtained if the mixture of the liquids is passed twice through the mill, or even through two mills in series.

Power Consumption

No figures are available for the power consumption on the turbine-driven mill. However, there are some on the motor-driven, 3000-r. p. m. mill, of which the following will serve to give some idea of the power required to drive the mill.

Running empty the mill requires 5 kw. With a charge of 1000 grams solid material and 4000 cc. water, the power consumed varies between 15.5 and 19.3 kw. The viscosity of the charge will change these figures and if the charge is reduced to one-half, the power consumed is about 10 to 12 kw. For emulsifying liquids less power is required, probably about 13 to 15 kw., and hence for 1.5 tons of liquid per hour the consumption would be about 4 to 5 watt-hours per pound.

Grinding Solids

For grinding solids the size of particle obtained depends on the ease with which the substance may be fractured and on the speed of the mill. Hence, for a given speed the size of the particle will vary from substance to substance and the uniformity of the product will depend on the length of time it is beaten. There are very few data available on the actual particle size of materials which have been ground in the Plauson mill. However, in most cases the substances show a very decided Brownian movement when viewed in a microscope equipped with a dark, ground illuminator. Naturally, not all the particles show this movement, but a large percentage are of a size small enough to exhibit this phenomenon. At the same time, only a very small percentage, if any, of materials such as barytes, zinc oxide, lithopone, clay, etc., can be ground to the degree of fineness possessed by gas black. Von Hahn[1] has published some figures on the size of particles obtained in different gas blacks, but the figures given for the "American Gas Black" are obviously very far from the truth. This is because of the dispersion medium, 49 per cent alcohol, which will not disperse gas black, and hence all von Hahn's results were obtained on a sample which was badly agglomerated. The particles in ordinary American gas black are all less than 0.2 μ. However, the Plauson mill will grind most materials to a degree

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[1] *Kolloid Z.*, **31**, 96 (1922).

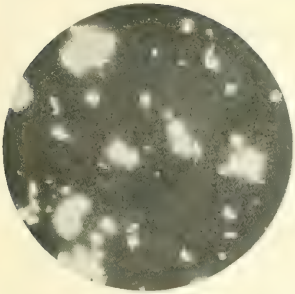


Fig. 1—Original China Clay. 270 ×

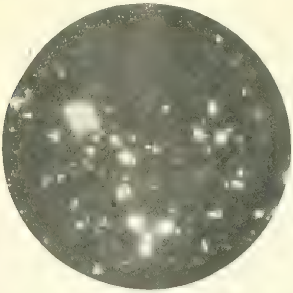


Fig. 2—China Clay Ground in 3000-R. p. M. Mill. 270 ×

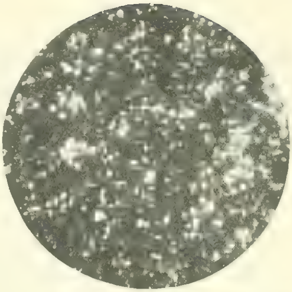


Fig. 3—China Clay Ground in 12,000-R. p. M. Mill. No Dispersator or Protective Colloid. 270 ×

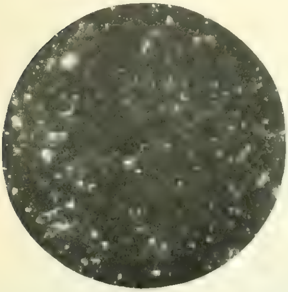


Fig. 4—China Clay Ground in 12,000-R. p. M. Mill with Dispersator and Protective Colloid. 270 ×

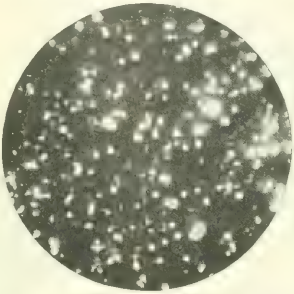


Fig. 5—Original Zinc Oxide. 405 ×

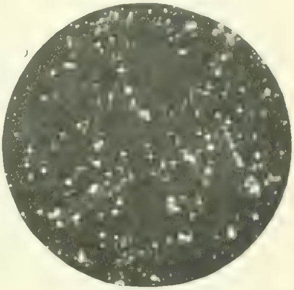


Fig. 6—Zinc Oxide Ground in 12,000-R. p. M. Mill. 405 ×

of fineness unattainable by other grinding machines. The claim is made that all materials can be reduced to a colloidal size in the mill, but the term colloidal is rather too elastic for the definition of particle size.

"Dispersators"

It is claimed by Plauson that the addition of certain substances in very small amounts will aid the grinding to a very marked degree. These substances are called "dispersators." In addition, a certain amount of a protective colloid, such as gelatin, gum arabic, lysalbinic, protalbinic acids, etc., is added. The function of the "dispersator" is to put an electric charge on the particle. It is well known that very small amounts of electrolytes are necessary to make a stable sol, and the "dispersator" is usually an electrolyte, such as sodium hydroxide, ammonia, etc., depending on the nature of the substance being ground. In some cases acids might just as well be used.

The photomicrographs show very well the effect of the grinding both with and without the dispersators. Fig. 1 is the original china clay which was used and Fig. 5 is the original zinc oxide. Fig. 2 shows the china clay after being subjected to the action of the 3000-r. p. m. mill for 10 minutes in the presence of a small amount of alkali as dispersator and gum arabic as a protective colloid. It will be seen that although the material is somewhat reduced in size the reduction is not very great. Fig. 3 shows the same material ground in the 12,000-r. p. m. mill without the use of dispersator or protective colloid. In order to obtain a comparative dispersion of the two clay samples both dispersator and protective colloid were added and stirred in *after* the sample was ground. Fig. 4 shows the same material ground with the dispersator and the protective colloid. A comparison of these two photomicrographs will show that the 12,000-r. p. m. mill has a decided effect in reducing the size of the clay particle, but that this size is independent of the presence of the dispersator or the protective colloid. With substances of a different nature and also of a small size originally the effect of the mill is not nearly so great. This can be seen from a comparison of Figs. 5 and 6, which show original zinc oxide and the same material after grinding in the 12,000-r. p. m. mill. The effect of the mill is clearly visible in each figure.

Chemical Reactions

Chemical reactions taking place between phases of heterogeneous system can be made to proceed more rapidly by increasing the interfacial area, and hence it is claimed by Plauson that many reactions which take place only very slowly or not at all can be made to go very rapidly in the colloid mill. One such reaction is the saponification of fats to make soap and this reaction is complete within 5 or 10 minutes when the alkali oil and water are beaten together in the 3000-r. p. m. mill. No external heating is necessary and the process might be made to give a continuous flow of soap from the mill. The time of reaction may be even less than 5 minutes, but it does take place in that time. The esterification of cellulose by acetic acid may also be accelerated by carrying it out in the Plauson mill after the cellulose has been reduced in size from the fiber to something considerably smaller. It is also possible that resins and gums could be dispersed in water or other media in which they are insoluble by passing them through the mill after adding sufficient solvent to soften them and thus change the action of the mill from that of grinding a solid to that of emulsifying two liquids.

There are many places where the mill can be used in the chemical industry provided the cost of driving it is not excessive for the product. It has two main disadvantages at present—first, the power required to operate it, and, second, its small capacity. It is quite possible that its capacity and efficiency may be increased to the point where the cost per unit of material obtained will put the mill on a plane where it can be used commercially. There is a great deal of development work to be done, but this will probably be done best by the different industries themselves, as they are better acquainted with their own problems than any outside firm could possibly be. It is up to the individual firm to decide whether or not it will pay to develop it to meet the conditions under which it will have to operate.

Concentration Factor in the Combination of Tannin with Hide Substance[1]

By Arthur W. Thomas and Margaret W. Kelly

Columbia University, New York, N. Y.

The effect of time of reaction and concentration of the vegetable tannins gambier and quebracho upon the combination of tannin with hide substance was shown in an earlier paper.[2] The results given herein continue this investigation, including extracts of barks of hemlock, larch, oak, and wattle.

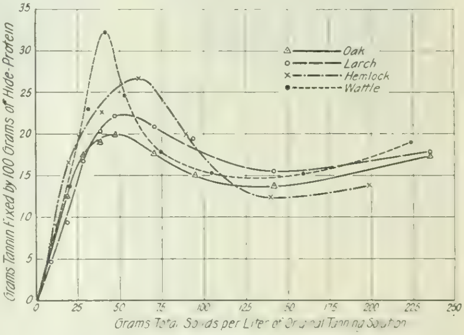
The method used was identical with that described in the earlier paper[2] except that portions of defatted hide powder (sifted to remove all particles finer than 100 mesh) equal to 5 grams of anhydrous substance were used, and the time of contact was set at 24 hours. The hydrogen-ion concentrations of all solutions were adjusted electrometrically to pH = 5, using sodium hydroxide.

For economy of space all data incidental to the analyses by the original Wilson and Kern method[3] are omitted. The fixation of tannin has been calculated to grams tannin combined per 100 grams hide protein, and plotted against concentration of the vegetable tanning extracts in terms of grams total solids per liter of solution, as shown in the curves.

The tannin content of each extract was determined by the modified Wilson and Kern method,[4] and for the purpose of studying the fixation as a function of the concentration of tannin, the following data are submitted:

Extract	Tannin in Total Solids Per cent
Oak	20.6
Larch	20.6
Hemlock	27.2
Wattle	30.4

The sharp maximum previously shown by quebracho[2] is found here with each extract studied. The decrease in fixation following increased concentration of tanning solution was tentatively explained in the earlier paper as due to heavy surface tannage, thus impeding the diffusion of uncombined tannin into the interior of the hide-powder particles. In addition to this it should be noted that decreased rate of fixation with increasing concentration of tanning solution is predicted by the Procter-Wilson theory. The rate of fixation is at a maximum where the positive charge of the collagen and the negative charge of the tannin particles are at their maximum. Now increase of electrolyte concentration resulting from increased concentration of the tanning extract will reduce the potential of the collagen. Likewise, the negative potential difference of the tannin particles decreases with increase in concentration, as experimentally demonstrated by Thomas and Foster[5] in the case of quebracho. Furthermore, the decreasing degree of dispersion of the tannin particles causes a decrease in the rate of diffusion of the same. Since in all cases the reaction of the solutions was adjusted to pH = 5, the charge of the collagen would be at its minimum, and consequently the downward slope of the curves could be ascribed almost entirely to the changes in potential difference and degree of dispersion of the tannin particles.



The "gelatin-salt" test for detection of tannin was applied to all filtrates in the fixation experiments plotted above, and showed complete removal of tannin by the hide substance up to the maximum points in all curves, and where more tannin was present than could be fixed by the hide, the curves rapidly sloped downward. In other words, the maximum points were obtained with amounts of tannin in the solutions which corresponded to the saturation point of the hide substance for the particular tannin, and this was in the range of 10 to 17 grams of tannin per liter of solution.

The order of magnitude of the maxima is in the order of the astringency of the tannins. It will be seen from inspection of the percentages of tannin in the extracts used that the order of relative proportion of tannin to non-tan is wattle > hemlock > larch = oak, while the order of the magnitudes of maximum fixation is wattle > hemlock > larch > oak.

The upward trend of the curves beginning at the concentration of 140 grams total solids per liter seems to be due to the accumulation of insolubles in these very concentrated solutions, which are not removed completely by the washing of the tanned samples with cold water.

The authors express their indebtedness to A. F. Gallun & Sons Co., for grants in aid of this investigation.

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[1] Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. Contribution No. 414 from the Chemical Laboratories, Columbia University.

[2] This Journal, **14**, 292 (1922).

[3] *Ibid.*, **12**, 465 (1920).

[4] *Ibid.*, **13**, 772 (1921).

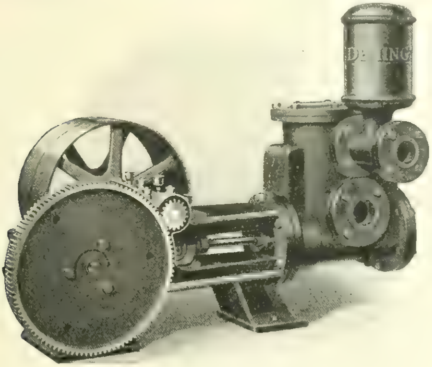
[5] This Journal, **14**, 191 (1922).

Pumps for Industrial Purposes

By W. F. Traudt

Taber Pump Co., Buffalo, N. Y.

THE pump is a vital part of many industrial processes and yet there is probably no piece of equipment which is purchased with so little consideration as to its application. There are an almost infinite number of combinations of mechanical elements which can be assembled into a pump design. It therefore becomes possible, by marshaling such elements properly, to build a pump which will meet an industrial problem more satisfactorily than "just a pump."



Piston Type Pump

There are many types of pumps, but such as are of industrial interest can, in a general way, be placed in four groups—namely, piston, plunger, centrifugal, and rotary. There are, however, many variations in design and construction in each group.

There are pumping problems for which a piston or plunger type pump is better suited than any other. There are also conditions where nothing will so satisfactorily fulfil the requirements as a centrifugal. Then again, there is a combination of circumstances surrounding a pumping problem which cannot be better taken care of than through the medium of a rotary pump; thus, applying the pump to the job.

If a fluid has the consistency of water or is no more viscous than light motor oil, then a centrifugal pump can be applied with success. Whether the centrifugal pump should be of the single or double-suction type, or equipped with open or enclosed impellers, depends upon circumstances surrounding the installation, such as volume in gallons per minute, head in feet, and the method available for driving the pump. In general, it can be stated that for large volumes at low head a single-suction, open impeller type pump is usually satisfactory, while for high heads the double-suction, enclosed, impeller type centrifugal pump is more efficient.

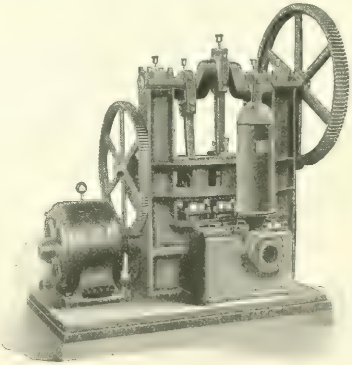
A small volume, say 50 gallons per minute, and a high head, 50 to 75 pounds per square inch, is a combination of conditions which can be better met with a piston or plunger type pump than a centrifugal, unless there is some very special reason why a centrifugal pump should be considered. Such a reason might be found in passing certain kinds of fluids through filter presses, because the centrifugal pump has the advantage of delivering a steady flow without any pulsations or shocks through the filter medium. It also has the advantage that as the filter becomes clogged, the rate of flow will automatically adjust itself to the increased filter resistence, and no undue pressure will accumulate on the filter with the possibility of rupturing the cells or the filter itself. A plunger pump will deliver a relatively small volume of fluid against a high head more economically than either a centrifugal or a rotary pump. A rotary or plunger type pump will handle viscous materials which would be impossible with a centrifugal. A rotary pump designed for the purpose will handle materials which are too viscous for either a plunger or piston type pump (materials like white lead paste, etc.). It must, however, be borne in mind that such materials cannot be handled by an ordinary rotary pump. It must be designed for the purpose in order to assure success.

The fact must not be lost sight of that there is no universal rotary pump. In fact, there is no universal pump of any type. It follows that each type or design of pump is limited to certain uses. These limitations are governed by a variety of conditions, but fundamentally the viscosity, temperature, volume, head, and chemical properties of the fluid are most important.

Effect of Viscosity of Fluid

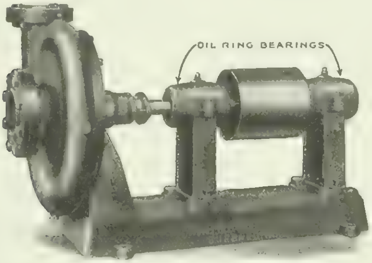
When using the term "fluid," every substance is included which is plastic enough to permit it to flow through a pipe—for example, commercial white lead and oil, cereal mash, chilled lard, tooth paste, paper pulp, pitch, tar and asphalt, chocolate paste, glucose, molasses, etc.

Good practice would dictate that viscous materials must either gravitate or be fed to the pump inlet. Such materials do not respond readily to suction lifts, as they have a high coefficient of friction; therefore, one must avoid trying to impart an excessive velocity of flow to them through any part of the pumping system. A pumping system here refers to the whole equipment from the source of supply to the point of discharge, including the vessel, agitator or equivalent in which the source of supply originates, and the



Triplex Plunger Pump

container into which it is to be delivered. If a paste or viscous material can attain a normal (efficient) velocity of 0.5 feet per second the pumping system should be so arranged that in no part of it a greater velocity is attempted than the ideal condition would include, not even through the pump, its ports or valves. Thus, a 3-inch pump might efficiently handle 300 gallons per minute of a fluid of low viscosity, and yet not more than 10 gallons per minute could be successfully handled when the material is highly viscous.



Open Impeller Type Centrifugal Pump

A pump speed or capacity must be synchronized with the fluid's economical flowing capacity, and all pipes and fittings used in the pumping system must also be of such sizes to accommodate the economical flowing capacity of the material pumped. If a pump has a capacity too large for the normal rate at which a viscous fluid will flow, there will be a tendency to "wire draw" the fluid in the suction pipe and set up a high vacuum in the same. This will result in having the pump's displacement only partly filled and under vacuum, causing shocks and setting up serious vibration and noise in either piston, plunger or rotary type pumps. The reason for this condition is obvious. It will be seen, therefore, that it is imperative to avoid all attempts to pump a viscous fluid faster than its viscosity will permit it to flow.

Effect of Perfect Vacuum

Too few people realize that even if a pump were able to produce a perfect vacuum on the suction side, the only head pressure forcing the fluid to the pump would be equal to that of the atmosphere, provided the source of supply was on the same level as the inlet to the pump. It would be considerably less, however, with a vertical suction lift, and as much less as the static head resulting from a lift below the level of the pump inlet.

A practical example might be suggested by assuming 100 feet of straight 1-inch pipe connected to the discharge of a pump. This line of pipe would require a head equal to approximately 12 pounds per square inch to force water at the rate of 20 gallons per minute through it, because the velocity set up in the pipe requires this pressure to overcome the frictional resistance.

Should it be required of a pump to draw water to the inlet, a vacuum of approximately 25 inches would have to be created by the pump to cause a flow of 20 gallons per minute through a 1-inch straight pipe 100 feet long. If the water were warm or saturated with air, it is obvious that such a vacuum could not be maintained, and thus the capacity would be less. If the suction pipe line were longer, the rate of flow could not be established because of the increased friction resulting. It follows that the pump cylinder would then only be partly filled with water while the balance of the space would be under vacuum. Such a condition would cause shock within the pump as well as the pipe line, resulting in noise and vibration which might cause serious difficulty.

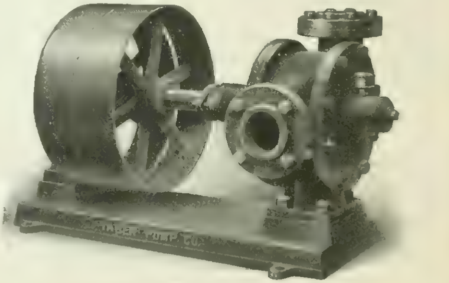
This being the condition with water, how much more care must be exercised when given a viscous material to handle, the coefficient of friction being many times greater than that of water.

Relation of Pump Efficiency to Plant Efficiency

Efficiency is always an important item to be considered in the selection of pumps or any other equipment, but the meaning of efficiency must be applied in its broadest sense—that is, the ultimate efficiency as related to other equipment in the process or plant—namely, freedom of interruptions, etc. A pump may have a very high mechanical efficiency in itself and yet be the cause of great inefficiency in the plant or process as a whole, while a pump of low mechanical efficiency may bring up the plant efficiency to an exceedingly high level. Some concrete experiences will illustrate this statement.

In a plant handling liquid foodstuffs an excellently made and efficient pump was used and would have been correctly applied if the fluid had been of a kind where the element of cleanliness was not important. But the pump was of such construction that accessibility to the interior, ports, etc., was impossible, thus permitting the breeding of bacteria, which seriously impaired the flavor and quality of the product. The difficulty was overcome by building a special type of open impeller centrifugal pump in which the features making for higher efficiency had to be sacrificed in favor of obtaining the essential sanitary features. Thus, a higher efficiency was established within the plant by the application of a pump of lower efficiency, but sanitary in construction.

In a certain chemical industry in which a great many pumps were installed, continual interruptions were experienced because a standard open impeller type pump had to be used, and since the service was continuous some of these pumps would wear out within from four days to a week. The material to be handled was not only of an acid nature, but held in suspension materials which were highly abrasive. The pumps were operated at the most efficient speeds considered strictly from a hydraulic standpoint. The pressure heads were relatively high and required high speeds to obtain good mechanical efficiency. The writer was consulted on the matter and advised that improvement could only be obtained by using larger pumps and operating them at slower speeds, which in some instances reduced the mechanical efficiency of the pump unit to half, with the result that shutdowns and interruptions were reduced. Thus, the total plant efficiency was improved.



Rotary Pump Belt Driven

In one case, with a pump which had to be replaced every week, the time was extended to a month's operation before repairs or replacements had to be made; and in another instance, by changing the alloy from which the pump was made the service was extended from five weeks to eleven months. Therefore, it is very evident that the application of efficiency must receive the broadest consideration.

Thus, again, the importance of careful selection and application is obvious.

Unusual Forms of Pumps

If the subject of pumping fluids is given a little earnest thought, it is amazing to find how dependent upon some form of pumping operation the world is.

A siphon is a pump. Capillarity is a form of pumping and is frequently the only means by which line shafts are lubricated. Vegetation itself depends upon the pumping operation such as is accomplished through the rootlets of trees conveying moisture to the smallest twig and leaf. In short, any process which will cause a fluid to be raised from one point to another at the same or higher level can be considered a pumping system. Those who are interested in familiarizing themselves with the historical development of pumps will find a brief outline of the subject as practiced in the earliest stages of civilization in a book by Arthur M. Green on "Pumping Machinery."

It follows, therefore, that if one will consider industrial pumping problems with more care, and examine into all phases of the proposed pumping system, never losing sight of the physical and chemical properties of the fluid to be handled, there will result incalculable savings, not only in fuel or power, but through fewer interruptions in manufacturing processes. Too often when laying out an industrial process, one thinks of the pump at the "eleventh hour," and then only in terms of "just a pump."

Detector for Water Vapor in Closed Pipes[1]

By E. R. Weaver and P. G. Ledig

Bureau of Standards, Washington, D. C.

A simple device is described for determining the approximate concentration of water vapor in a gas. A glass tube is coated with platinum and the coating divided by etching into two electrodes. Platinum wires sealed through the glass connect the electrodes to a measuring circuit. The resistance to alternating current of a thin film of a hygroscopic electrolyte bridging the gap between the electrodes is used as the measure of the water vapor in the atmosphere with which the film is in contact. Sulfuric and phosphoric acids and various hygroscopic salts can be used in forming the conducting film. The detector is simple, rugged, and easily adapted for use in high-pressure piping and other situations in which the determination of water vapor is usually attended with difficulty.

Laboratory experiments showing the reliability, method of application, and limitations of the device are described.

THIS device was suggested by a description of the invention of Todd and Bousfield[2] for the same purpose. The apparatus described in the patent consists of two gauze electrodes separated by a layer of granular calcium chloride or other hygroscopic salt enclosed in a tube through which the gas is passed. The contents of the tube remain nonconducting so long as the calcium chloride is dry; but in the presence of much water vapor the granules become coated with a continuous film of solution which establishes electrical connection between the electrodes and gives an indication of the moisture present. A somewhat different arrangement was used by Paul Anderson,[3] who dipped the ends of two wires into the fused salt and exposed the bead of adhering salt to the gas to be tested. Two objections to these arrangements which it seemed possible to overcome are (1) the time and the amount of water required to produce a definite effect, and (2) the difficulty of restoring the detector to its original condition for further testing. In addition the device of Todd and Bousfield requires a definite circulation of gas through the tube.

These objections are largely eliminated in the present apparatus (Fig. 1), which is made of a piece of straight glass tubing sealed at one end. Near the closed end two platinum wires are sealed through the glass and fused against the outer surface of the tube, which is then frosted with a paste of barium sulfate and ammonium fluoride. The ends of the platinum wires inside the tube are soldered or fused to copper leads. The outside of the cell is carefully platinized by applying a colloidal solution of platinic chloride in lavendar oil, as described by McKelvey and Taylor.[4] This process is repeated until the layer of platinum is entirely smooth and continuous, care being taken that the platinized surface is in good contact with the electrode wires. The tube is then coated with paraffin and a line etched around it between the two electrodes with hydrofluoric acid to break the continuity of the platinum surface. On this narrow surface of separation and extending over the platinized electrode surfaces on both sides is painted a dilute solution of some hygroscopic electrolyte. In order to prevent motion which might break the leads, and at the same time to assure good insulation, it is well to fill the tube with melted paraffin and allow it to solidify.

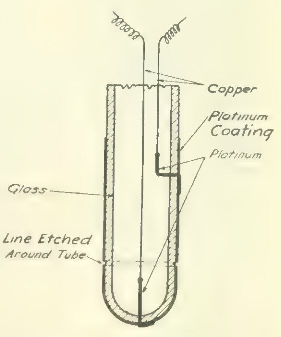


Fig. 1 Detector for Water Vapor. The Size of the Tube Is of Little Consequence. Those Employed in the Laboratory Have Usually Been Made from Tubes of Any Convenient Length, Having about 8 Mm. Outside and 5 Mm. Inside Diameter

The tube is then mounted in any suitable way (by passing through a paraffined cork stopper for ordinary laboratory work at atmospheric pressure) with the prepared end of the tube exposed to the gas to be tested. The resistance to an alternating current of the film bridging the "scratch" between the electrodes is a measure of the concentration of water vapor present.

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[1] Received July 7, 1923. Published by permission of the Director, U. S. Bureau of Standards.

[2] British Patent 137,547 (1920).

[3] *J. Chem. Soc.* (*London*), **121**, 1153 (1922).

[4] *J. Am. Chem. Soc.*, **42**, 1366 (1920).

Experimental

For the purpose of studying the device in the laboratory, such a detector was used in the manner shown in Fig. 2. The detector was mounted in a tube of slightly larger diameter, through which the gas to be tested could be streamed, and was set up either in a constant temperature bath or in the open air of the room. The electrical circuits are shown diagrammatically in the figure. The detector formed one arm of a Wheatstone bridge employing 15-volt, 60-cycle alternating current and an alternating current galvanometer in the measuring circuit. The alternating current galvanometer used, when connected to a source of 110-volt alternating current, supplied 15 volts (or lower potentials) directly from a "drop coil."

The detector was exposed to atmospheres of known moisture content by bubbling air through sulfuric acid solutions of various concentrations. The solutions were made by diluting ordinary C. P. sulfuric acid with distilled water, were cooled to 20° C., their density determined by the use of hydrometers giving readings accurate to the third decimal place, and the percentage of acid taken from the density table in *Circular* **19** of the Bureau of Standards.

The water vapor pressures of the solutions were obtained from the data of Regnault.[6] The air was saturated to the water vapor pressure of the solutions by bubbling it through the solution in a Greiner-Friedrich spiral wash bottle; it was then passed directly to the tube containing the detector.

The first work with a detector of this form was done in 1919. Two hygroscopic substances were used, phosphoric acid and rubidium carbonate, the latter being employed because it would not be greatly affected by traces of either carbon dioxide or ammonia. It was at first hoped that the method could be made accurately quantitative. When it became certain that this could not be done, the work was abandoned; but one of the detectors with a coating of phosphoric acid was left in place in the tube in which the test was made and stored in the laboratory for a period of three years. The gas inlet and outlet were open to the air during that time. Because of recent inquiries from different sources for means of detecting moisture, particularly in gases compressed for liquefaction, it seemed worth while to renew the investigation of this detector. Without renewing the original phosphoric acid coating, the detector which had been stored for three years was tried and found to be as sensitive as ever. This is excellent evidence for the reliability of the device as a detector of unusual and undesirable operating conditions, which will probably be its principal use.

In addition to phosphoric acid and rubidium carbonate, sulfuric acid, a mixture of sulfuric and phosphoric acids, calcium chloride, and sodium and potassium hydroxides have been tried as hygroscopic electrolytes, using the same detector tube.

When renewing or changing a coating of electrolyte, the detector tube was first carefully washed and dried. A thin gelatin solution, of about the consistency of good ink, was prepared and to it enough of the hygroscopic electrolyte added to make approximately a 1 per cent solution. This solution was applied to the surface of separation between the electrodes with the tip of a camel's-hair brush barely moistened with the solution, and quickly dried by passing dry air over it.

Discussion of Results

The attempts to use the alkaline hydroxides as hygroscopic coatings were not a success, because the resistances of the films never approached equilibrium but continually increased. This is believed to have been caused by a small amount of carbon dioxide (or possible other acid vapors from the sulfuric acid) which remained in the air stream in spite of some effort to eliminate it.

With any one electrolyte the resistance of the detector can, of course, be varied over a wide range by changing the strength and amount of the solution applied. The *relative* resistances when in equilibrium with atmospheres of different humidities are reasonably independent of the amount of

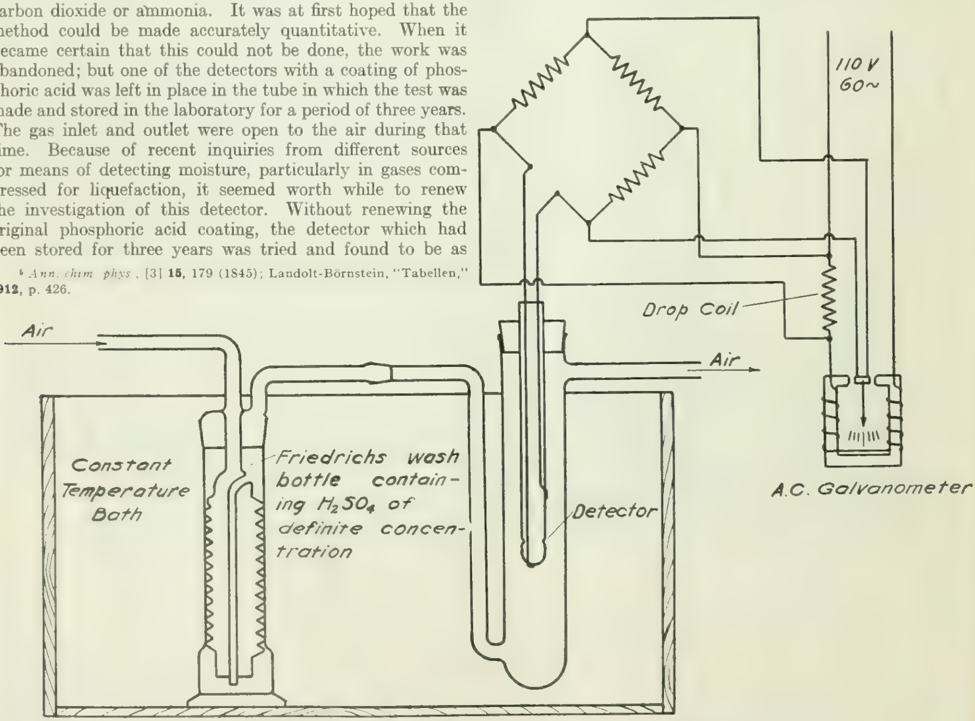
110 V
60~
Drop Coil
Air
Air
Constant Temperature Bath
Friedrichs wash bottle containing H_2SO_4 of definite concentration
Detector
A.C. Galvanometer

Fig. 2—Simple Arrangement of Apparatus for Laboratory Study

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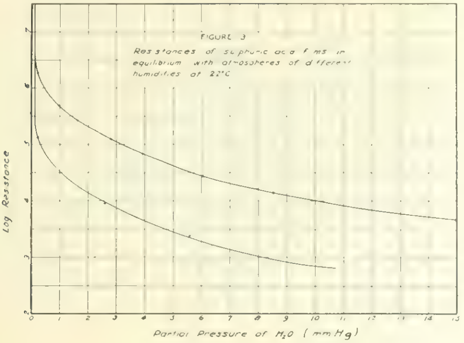
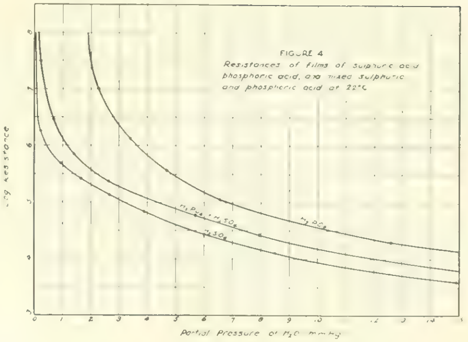
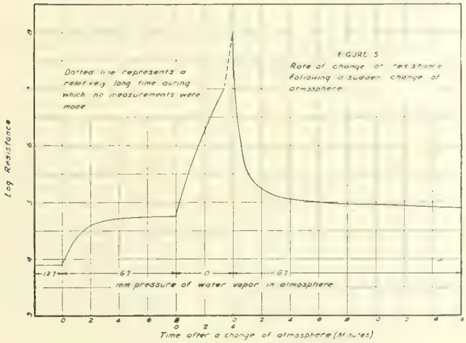
[6] *Ann. chim. phys.*, [3] **15**, 179 (1845); Landolt-Börnstein, "Tabellen," **1912**, p. 426.







electrolyte in the film and dependent only upon the hygroscopic substance used. How closely this relation applies is indicated by Fig. 3, which shows the observed resistances of two coatings of sulfuric acid. One had 13.5 times the resistance of the other. The upper curve is drawn through the points representing the observed resistances of the thinner coating. The lower curve is then drawn 1.3 divisions on the logarithmic scale (log 13.5 = 1.3) below the upper one. The circles near the lower curve represent observed data on the thicker coating and indicate the close agreement with the rule stated.

Fig. 4 shows the resistance curves for films of sulfuric acid, phosphoric acid, and a mixture of sulfuric and phosphoric acid containing about equal weights of each. This mixture was prepared in the hope of extending the range within which a given film could be used for semiquantitative work. The rate at which changes of resistance take place when the humidity of the atmosphere is changed depends greatly upon the thickness of the hygroscopic film. The behavior in this respect of the three-year-old phosphoric acid coating is shown in Fig. 5. The readings were made by two observers, one of whom observed resistances while the other noted the stop watch and recorded readings. In the middle range of resistances about 2 hours were required to so nearly attain equilibrium that no further change of resistance could be noted by the rather sensitive method of measurement employed; but the change which took place after the first 5 minutes had little practical significance. On changing from an atmosphere containing about 0.9 per cent water vapor to a dry atmosphere, the resistance increased about one hundredfold in the first minute. On changing back to the former atmosphere, the resistance decreased to about one seven-hundredth of its maximum value in one minute. The resistance changes of the sulfuric acid film represented in Fig. 4 were even more rapid.

Probably the greatest drawback to the extensive use of the detector for quantitative work is the narrow range of high sensitivity for any one substance, 0.1 to 5 mm. of water vapor pressure for sulfuric acid, 2 to 10 mm. for phosphoric acid, and even narrower ranges for salts like rubidium carbonate and calcium chloride. The sensitive range of rubidium carbonate is slightly higher than that of phosphoric acid (it was not very accurately determined); that of calcium chloride is in the neighborhood of 15 mm.

It was found to be impossible to let a film come to equilibrium with an atmosphere containing much water and to subsequently reproduce the resistance readings earlier obtained at low humidities. In every case, the resistance increased under such conditions. It appears probable that the electrolyte flows off the surface of the cell when it is allowed to absorb too much water. But if the coating is kept dry, or not far from its sensitive range, resistance readings are quite uniform and reproducible.

Another important disadvantage of the detector is the large effect of temperature. In the case of phosphoric acid and the hygroscopic salts, an increase of temperature expels water from the film and greatly increases its resistance. With sulfuric acid films the effect of temperature upon the composition of the film and the resistivity of a solution of given composition are more nearly balanced and the resultant coefficient is not nearly so great.

The curves for sulfuric and phosphoric acids in Fig. 4 can be used in connection with a single determination of resistance at known humidity to establish a calibration curve for any detector using the same compounds at about the same

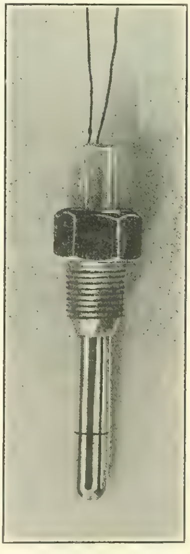


FIG. 6—DETECTOR PREPARED FOR INSERTION INTO A PIPE LINE AT HIGH PRESSURE

temperature, 22° C. If, for example, a detector with a sulfuric acid film which showed a resistance, R, in an atmosphere known to have a water vapor pressure of 5 mm. shows a resistance of 10 R when placed in a pipe line, it can be seen at once from the curve that the pressure of the water vapor in the pipe must be about 1.1 mm. A resistance of 100 R would correspond to a vapor pressure of 0.1 mm.

In case such a detector is used regularly it should be checked frequently by exposing it to an atmosphere of known humidity. It is especially necessary to make this check after the detector is known to have been in an atmosphere of unusually high humidity. The coating should be replaced whenever there is reason to suspect that appreciable chemical change has taken place or when the resistance is no longer in the most easily measurable range.

Fig. 6 shows a detector prepared for insertion into a pipe line at high pressure. The glass tube is platinized and soldered into the steel bushing by the method described by McKelvy and Taylor.[4]

If the same device were combined with means for regulating and measuring temperature, it could certainly be used for fairly accurate quantitative work at any range of humidity by selecting the proper electrolyte. If, for example, an entirely nonhygroscopic salt of slight solubility were used for coating and the resistance always brought to a definite value by changing the temperature, the apparatus would be practically a dew point apparatus of small size on which the first trace of condensation would be detected by a much more sensitive and generally applicable method than direct vision. In this form the apparatus could be located at a place inaccessible for visual observation and its indications recorded electrically if desired.

Investigation of the Hypobromite Method for Determining Bleach Requirement of Pulps[1]

By T. M. Andrews and M. W. Bray

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Tingle's hypobromite method for determining the bleach requirements of pulps has been tried under varying conditions on sulfite and soda pulps. It was found necessary, in order to avoid errors due to volatilization of the bromine, to dilute the reacting solution and to maintain the temperature between 23° and 28° C. For sulfite pulps the method is of definite value provided the necessary precautions, as pointed out, are properly observed and the variations in bleach requirements are not too great. For soda pulps the method cannot be recommended without further investigation, owing to an apparent lack of constancy in the ratio of the chlorine factor to the bleach required.

TINGLE recently worked out a rapid method for the determination of the bleach requirement of pulp by the use of hypobromite solution.[2] He found that by using a factor the results agree closely with the bleach used in the mill. His results are based chiefly upon tests made on a single type of sulfite pulp and under conditions peculiar to his own laboratory. This investigation was undertaken in order to determine the reliability of this test when applied to various kinds of pulps and under varying conditions not specified by its originator.

Tingle's method is briefly as follows:

> A sample of 0.6 to 0.75 gram of oven-dry pulp is dissolved in 30 cc. of a mixture consisting of nine parts by volume of hydrochloric acid (sp. gr. 1.19) and one part of sulfuric acid (sp. gr. 1.84). To this solution are added 20 cc. of 0.1 N sodium hypobromite. After standing 30 minutes the excess bromine is back-titrated with 0.1 N thiosulfate solution, and the results are calculated in terms of grams of chlorine per 100 grams of pulp, designated the chlorine factor. By means of an empirical factor ($K = 3$) the chlorine factor is converted into bleach required to bring the pulp to a standard white color. The acid solvent and the standard solutions used in these tests were the same as those used by Tingle.

In Tingle's article it is stated that only oven-dry pulp can be used. The pulps used in the investigations at this laboratory have contained as high as 7.9 per cent moisture, and this can probably be increased to 10 per cent without too great a dilution of the acid solvent. Those with a higher moisture content may be quickly dried to less than 10 per cent moisture, and the moisture accurately determined while the analysis is being carried out.

One difficulty inherent in this method is that the sample is too small to be thoroughly representative of a large amount of pulp. The size of the sample can hardly be increased, however, with any method making use of the solvent employed. By raising the temperature to 50° C. a larger quantity may be dissolved, but this gives rise to serious errors and the results are entirely unreliable. Ordinary variations in room temperature while dissolving the pulp do not appreciably affect the analytical results. If careful methods of sampling are followed, the errors due to sampling should not be appreciably greater than those incident to other laboratory methods for determining the bleach requirements.

Another difficulty with Tingle's method is that it does not take into consideration the effect of temperature on the rate and extent of the reaction. Further, it is practically impossible to add the hypobromite solution to concentrated acid without losing some of the bromine. Again, upon dilution of this solution there is a further and much greater chance of losing a considerable portion of the bromine.

CALCIUM HYPOCHLORITE METHOD

It was found impossible to determine by actual mill operation the bleaching powder requirements of the pulps used in this investigation. They were tested, however, by the method in regular use at the Forest Products Laboratory for the determination of the bleach requirements by actual calcium hypochlorite bleaches. This method consists in subjecting about 60-gram samples of each pulp to varying amounts of bleach in warm dilute solution with constant stirring until exhausted. The bleached pulps are washed, made into hand sheets, dried, and compared with a standard. The standard for sulfite pulp was a high-grade, commercially bleached spruce pulp, and for soda pulp a typical, commercially bleached aspen soda pulp.

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[1] Received March 30, 1923. Presented before the Division of Cellulose Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Paper*, **29**, 7 (1922); THIS JOURNAL, **14**, 40 (1922).

EXPERIMENTAL—Seven sulfite and two soda pulps were analyzed under various conditions. The results of these analyses are given in Table I. In all these 20 cc. of hypobromite were added to a concentrated acid solution of the pulp and allowed to act for 30 minutes. The first two sets of analyses, on Nos. 104 and 101, were carried out under conditions identical with those employed by Tingle, and the results do not check well among themselves. With No. 104 there is a variation of 5.9 per cent in the amount of bleach required, and with No. 101 more than 2.0 per cent.

TABLE I—BLEACHING POWDER REQUIRED FOR SULFITE AND SODA PULPS AS DETERMINED BY TINGLE'S HYPOBROMITE METHOD UNDER VARIOUS CONDITIONS

(0.6-gram sample, 20 cc. hypobromite, acting for 30 minutes)

No.	Temperature ° C.	Moisture %	0.1 N Hypobromite Consumed Cc.	Bleaching Powder Required: Hypobromite Method %	Bleaching Powder Required: Forest Products Laboratory Method %
			Mitscherlich Sulfite Pulp—Spruce Wood		
104	Room	6.8	4.63	25.2	30
			4.72	25.7	
			5.36	29.1	
			5.71	31.1	
				Av. 27.8	
101	Room	6.4	2.17	11.8	15
			2.50	13.5	
			2.55	13.8	
				Av. 13.0	
103	23	6.6	2.28	12.5	12
			2.44	13.2	
			2.28	12.5	
			2.33	12.8	
				Av. 12.8	
103	23	O. D.[a]	2.51	12.9	12
			2.44	12.4	
			2.42	12.3	
				Av. 12.5	
103	28	6.6	2.61	14.1	12
			2.73	13.0	
			2.77	12.3	
				Av. 13.1	
103	28	O. D.	2.92	14.8	12
			2.71	13.7	
			2.71	13.7	
			2.61	13.2	
				Av. 13.8	
104	Room	6.8	5.71	31.1	30
			5.88	32.0	
				Av. 31.5	
103	5	6.6	1.19	6.5	12
			1.00	5.4	
			1.27	6.9	
				Av. 6.3	
103	18	6.6	1.98	10.8	12
			1.79	9.7	
			1.68	9.1	
				Av. 9.9	
37	23	4.1	8.39	44.4	Greater than 30
			8.01	42.5	
				Av. 43.5	
61	23	4.9	6.70	35.6	Greater than 30
			6.70	35.6	
			6.90	36.7	
				Av. 36.0	
51	23	3.2	13.92	73.0	
			13.46	70.1	
			13.61	71.3	
				Av. 71.5	
99	23	6.8	2.74	14.9	15
			2.67	14.5	
			2.82	15.4	
				Av. 14.9	
			Quick Cook Sulfite—Spruce Wood		
29	23	4.4	2.13	11.3	12
			2.23	11.8	
			2.23	11.8	
				Av. 11.6	
			Soda Pulps—Aspen Wood		
94	23	5.6	2.72	14.6	18
			3.05	16.4	
			2.77	14.7	
				Av. 15.2	
116	23	6.2	1.88	10.1	26
			2.03	10.9	
				Av. 10.5	

[a] O. D. = oven-dried.

Pulp No. 103 was analyzed under the same conditions, except that the temperature was kept at 23° C. during the period of the reaction with the hypobromite and the results were not so varied. This same pulp, previously dried in the oven, gave results that were in close accord with those obtained with air-dried samples containing 6.6 per cent moisture.

TABLE II—EFFECT OF RATE OF ADDING HYPOBROMITE SOLUTION TO CONCENTRATED ACID ON THE LOSS OF BROMINE BY VOLATILIZATION IN BLANK TESTS

RATE OF ADDING HYPOBROMITE	Hypobromite Cc.	0.1 N Thiosulfate Cc.
Normal	20.01	19.03
	20.03	18.48
	20.04	18.54
	20.07	18.83
	20.05	18.78
	20.04	18.93
Two-thirds Normal	20.00	17.79
	20.00	18.15
	20.00	18.05
One-third Normal	20.00	16.90
	20.00	16.56
	20.00	17.00
	20.00	16.85

TABLE III—TITRATION OF HYPOBROMITE THAT HAS BEEN ADDED TO DILUTED ACID

Hypobromite Cc.	0.1 N Thiosulfate Cc.
10.00	10.08
10.00	10.09
10.00	10.00
10.00	10.02
10.00	9.97
10.00	9.95
10.00	9.87
10.00	9.82
10.00	10.00
10.00	10.00

The temperature at which the hypobromite reacts with the pulp exerts a decided influence. At 5° C. the bleach values varied between 5.4 and 6.9 per cent. At 18° C. they approximated 9.9 per cent and at 23° C., 12.8 per cent. A further increase of 5° C., however, causes a rise of only 0.3 per cent in the bleach value. The results of these analyses are shown by Curve A, Fig. 1.

TABLE IV—BLEACHING POWDER REQUIRED FOR MITSCHERLICH SULFITE SPRUCE PULPS BY THE HYPOBROMITE METHOD, USING DILUTED ACID SOLUTION OF PULPS UNDER VARYING CONDITIONS

(0.6-gram sample)

No.	Temperature ° C.	Moisture %	0.1 N Bromine Solution Added Cc.	Time of Reaction Min.	0.1 N Bromine Consumed Cc.	Bleaching Powder Required: Hypobromite Method %	Bleaching Powder Required: Forest Products Laboratory Method %
103	23	6.6	20	30	2.81	15.3	12
					2.76	15.0	
					2.79	15.2	
						Av. 15.2	
103	23	6.6	5	30	1.73	9.4	12
					1.83	9.9	
					1.78	9.7	
						Av. 9.7	
103	23	6.6	10	20	2.12	11.6	12
					2.15	11.7	
					2.15	11.7	
						Av. 11.7	
101	23	6.4	10	20	2.86	15.5	15
					2.76	15.0	
					2.76	15.0	
						Av. 15.1	
101	23	6.4	10	30	2.88	15.6	15
					2.91	15.7	
						Av. 15.7	
101	23	6.4	10	40	2.98	16.2	15
					3.02	16.4	
						Av. 16.3	
101	23	6.4	10	90	3.10	16.8	15
					3.07	16.7	
					3.07	16.7	
						Av. 16.7	
101	23	6.4	10	120	4.18	22.6	15
					3.83	20.8	
					3.68	20.0	
						Av. 21.1	
101	18	6.4	10	20	2.48	13.4	15
					2.43	13.2	
						Av. 13.3	
101	28	6.4	10	20	2.77	15.0	15
					2.76	15.0	
					2.76	15.0	
					2.67	15.5	
						Av. 15.1	

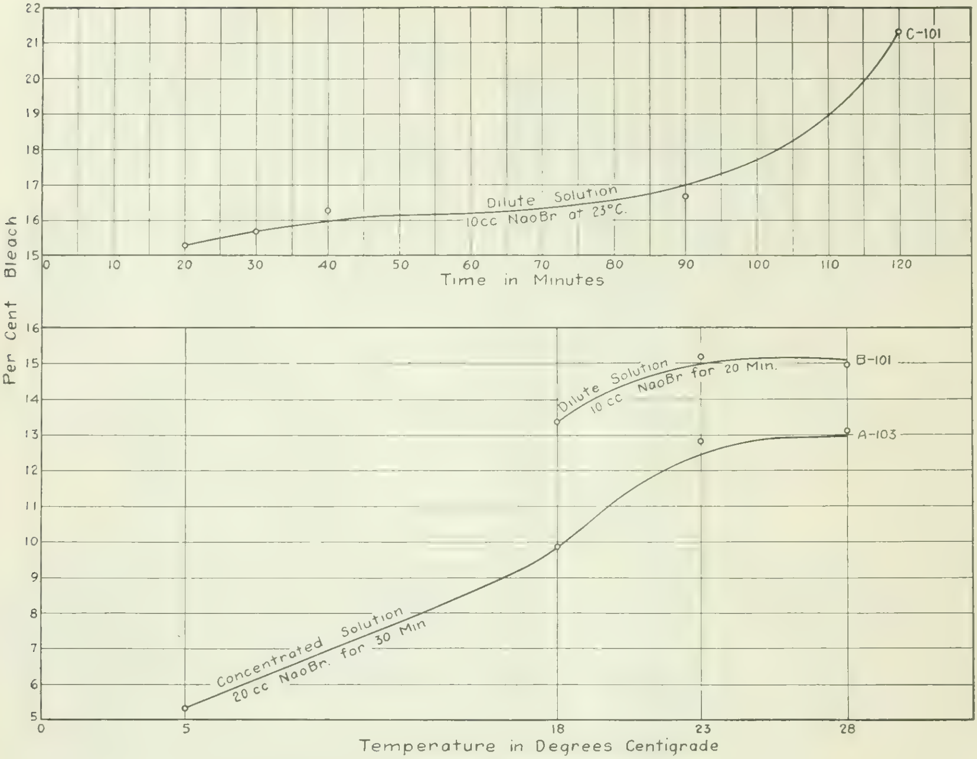

FIG. 1—RELATION OF TIME AND TEMPERATURE OF REACTION TO BLEACH REQUIRED

The errors due to losses of bromine by volatilization may be well illustrated by the results obtained in standardizing the hypobromite solution against 0.1 N thiosulfate solution, as given in Table II. These were all run in the same manner, time, and dilution as regular analyses, with the exception that the rate of adding hypobromite solution was varied.

By diluting the acid with 300 cc. of water prior to adding the hypobromite, the volatilization losses were reduced and more concordant results were obtained, as indicated by the results in Table III. Each pair of results was determined on different days and with a different strength of hypobromite solution.

Tingle's method was modified, therefore, by diluting the acid solution of the pulp with 300 cc. of water at the temperature desired for the reaction prior to the addition of the hypobromite. Several pulps were tested by this modified method under a variety of conditions. The results, given in Table IV, show the effect of time, temperature, and concentration of the reagent.

With 20 cc. of hypobromite acting in a concentrated solution for 30 minutes at 23° C., bleach values ranging from 12.5 to 13.3 per cent were obtained for No. 103. With dilute solution, under corresponding conditions, these values ranged from 15.0 to 15.3 per cent. By a similar treatment with 5 cc. of hypobromite bleach, values from 9.4 to 9.9 were obtained. Apparently, this concentration is not sufficient for the reaction. However, with 10 cc. of hypobromite acting for only 20 minutes, values from 11.6 to 11.7 were obtained, which are very close to 12.0 per cent as found by the Forest Products Laboratory method. Pulp No. 101 treated with 10 cc. of hypobromite for 20 minutes gave values from 15.0 to 15.5 per cent, which agree with the value obtained by the Forest Products Laboratory method.

Curve C, Fig. 1, shows the effect of time on the consumption of bleach. The reaction proceeds rapidly for the first 20 minutes and then continues slowly for the next 70 minutes. After 90 minutes a secondary reaction apparently sets in, causing a more rapid bromine consumption. For practical reasons the shortest time of reaction is desired. No appreciable advantage is evident in the use of a period longer than 20 minutes.

The effect of temperature was, therefore, determined, using 10 cc. of hypobromite for a period of 20 minutes. The results, Curve B, Fig. 1, show that a variation from 23° to 28° C. produced little effect upon the results. Decreasing the temperature below 23° C., however, rapidly reduced the rate of reaction.

The conditions for the analysis most favorable to secure reproducible results which are at the same time comparable with those obtained by the Forest Products Laboratory method, are to use 10 cc. of hypobromite with a dilute acid solution of the pulp and allow the reaction to proceed for 20 minutes at a temperature between 23° and 28° C. The following modified analytical procedure is, therefore, recommended.

TABLE V—BLEACHING POWDER REQUIRED FOR SULFITE AND SODA PULPS BY MODIFIED HYPOBROMITE METHOD

(0.6-gram sample, 10 cc. 0.1 *N* hypobromite solution, acting 20 minutes at 23° C.)

No.	Wood Species	Moisture %	0.1 *N* Hypobromite Consumed Cc.	Bleaching Powder Required: Hypobromite Method %	Bleaching Powder Required: Forest Products Laboratory Method %
			Mitscherlich Sulfite Pulps		
31	Spruce	4.4	3.85 3.95	20.4 20.8 Av. 20.6	24
120	Spruce	5.4	3.30 3.35	17.7 18.0 Av. 17.9	18
96	Spruce	7.9	2.50 2.48	13.8 13.7 Av. 13.8	12
101	Spruce	6.4	2.86 2.76 2.76	15.5 15.0 15.0 Av. 15.1	15
103	Spruce	6.6	2.12 2.15 2.15	11.6 11.7 11.7 Av. 11.7	12
149	Spruce	3.9	2.47 2.52	12.8 13.2 Av. 13.0	12
154	Spruce	4.3	2.67 2.67	14.2 14.2 Av. 14.2	15
			Quick Cook Sulfite Pulps		
22	Spruce	4.3	2.98 3.00	15.8 15.8 Av. 15.8	15
142	Jack pine	4.0	2.85 2.92	15.0 15.3 Av. 15.2	14
145	Jack pine	4.0	3.10 3.10	16.4 16.4 Av. 16.4	18
			Soda Pulps		
116	Aspen	6.2 6.2	2.01 2.05	10.9 11.1 Av. 11.0	18
94	Aspen	5.6 5.6	3.03 3.19	16.3 17.1 Av. 16.7	20
42	Aspen	3.9 3.9	1.63 1.66	8.6 8.7 Av. 8.7	..
17	Aspen	5.2 5.2	2.32 2.38	12.4 12.7 Av. 12.6	17
80	Jack pine	5.6 5.6	3.42 3.37	18.4 18.1 Av. 18.2	30

MODIFIED ANALYTICAL PROCEDURE

Place 0.6 to 0.75 gram of the pulp in a dry, 500-cc. bottle having a well-ground glass stopper. Add 30 cc. of the acid solvent consisting of nine parts by volume of hydrochloric acid (sp. gr. 1.19) and one part of sulfuric acid (sp. gr. 1.84), and shake from time to time for about an hour until the pulp is in solution. There is a certain amount of dark material that does not entirely dissolve. All hard pieces can be disintegrated with a glass rod. When solution is complete, bring to 23° C. and add 300 cc. water (23° C.), and shake thoroughly. Then add 10 cc. of alkaline, 0.1 *N* bromine solution (8 grams of bromine to 1000 cc. 0.1 *N* sodium hydroxide solution) down the side of the bottle, stopper, shake well, and allow to stand 20 minutes with occasional gentle agitation in a room at 23° C. or in a water bath at the same temperature. Stop the reaction by adding 2 grams of potassium iodine dissolved in 25 cc. water and titrate immediately with 0.1 *N* thiosulfate, adding starch indicator toward the end. Since iodine is adsorbed by the pulp, the thiosulfate should be added slowly just before the end of the reaction. The final end point is reached when only a cream-colored or white suspension remains. Results should check within a range of 0.1 to 0.5 per cent bleach.

Analyses of additional pulps were made to check this method, and the results are given in Table V. Duplicate tests show satisfactory agreement. In No. 31 there is a variation of 3.5 per cent from the results of the Forest Products Laboratory method, due possibly to the high amount of bleach required. Possibly, for pulps having a bleach consumption greater than 20 per cent either a larger amount of hypobromite or a larger factor will be necessary. With Nos. 96 and 120 there is a maximum variation from the results of the Forest Products Laboratory method of 1.8 per cent and 0.3 per cent, respectively. No. 22, a quick cook, shows a bleach value only 0.2 per cent less than the Forest Products Laboratory result.

The bleach requirements of the soda pulps, Nos. 116, 94, 17, and 80, were difficult to determine accurately by the Forest Products Laboratory method. The relation between these results and those in mill practice has not been as thoroughly established as for the sulfite pulps, so that variation between the two methods cannot be used as evidence against the values obtained by the hypobromite method. This is especially true in view of the splendid agreement (Table VI) of the results of duplicate tests by the latter method on the same pulp. The bleach requirement is relatively high for all the soda pulps tested, and it is possible that more hypobromite or different conditions of time and temperature will be necessary to give optimum results. These have not been further investigated.

TABLE VI—RATIO OF BLEACHING POWDER REQUIRED FOR SODA PULPS BY FOREST PRODUCTS LABORATORY METHOD TO BLEACHING POWDER EQUIVALENT OF HYPOBROMITE CONSUMED

Sample	Wood Species	Bleaching Powder Equivalent to Hypobromite Consumed A %	Bleaching Powder Required by Forest Products Laboratory Method B %	Factor B/A
116	Aspen	3.7	18	4.9
94	Aspen	5.6	20	3.6
17	Aspen	4.2	17	4.0
80	Jack pine	6.1	30	4.9

The use of the factor 3 for soda pulps indicates a bleach requirement too low in every case. Recalculation of the actual ratio between the bleach requirement as measured by the two methods gives values ranging from 3.6 to 4.9, which are far from constant.

CONCLUSIONS

Without further investigation the hypobromite method cannot be recommended for soda pulps. For sulfite pulps, however, the method can be expected to have definite value provided the various precautions suggested in the modified method are properly observed.

Advisory Board for Carnegie Institute of Technology

One of the most important recent developments at Carnegie Institute of Technology has been the organization of an advisory board of Pittsburgh business and scientific men to coöperate with the work of the Department of Mining and Metallurgy. C. W. Heppenstall, president of the Heppenstall Forge & Knife Company, has been elected chairman of this board. The immediate function of the advisory board will be to coöperate with the institute in the solution of current problems affecting the work of the Mining and Metallurgy Department.

Beginning with the next college year, the Institute of Technology announces that special courses for graduates of liberal arts and technical colleges will be given by the Department of Mining and Metallurgy. The purpose of these courses will be to train young men for jobs in the metallurgical and allied industries leading to positions of managerial, sales, and executive capacities. A consistent demand is being made in this and other iron and steel producing districts, for college men, particularly in the nontechnical capacities, from the lack of whom this industry has long suffered. The coöperation of the newly organized advisory board has already been provided in preparing the curricula for these courses.

Formation of Maltose in Sweet Potatoes on Cooking[1]

By H. C. Gore

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The presence of maltose in cooked sweet potatoes is shown by the agreement of the quantity of sugars determined by copper reduction with the quantities measured by polarization and by its isolation in crystalline form.

Sugar is not formed at the boiling point. It is formed very rapidly, although not instantaneously, during the initial stages of the digestive action.

UNTIL very recently W. E. Stone[2] was the only chemist who had reported on the changes in composition of sweet potatoes which occur during cooking. He showed that dextrin was formed, and that, while it was possible to isolate sucrose from raw sweet potatoes by allowing it to crystallize from the alcohol extract, sucrose could not be thus prepared from baked sweet potatoes.

It has been shown by the writer[3,4] that sweet potatoes are rich in diastase and that upon slowly cooking Porto Rico potatoes nearly all of the starch changes into dextrin and maltose. Magoon and Culpepper[5] found that similar changes occur in sweet potatoes during canning.

The work described below shows that maltose, the sugar always formed in the saccharification of starch by diastase, forms in large quantity during cooking. The increases in sugars calculated as maltose, determined by copper reduction, agree substantially with the increases in sugar determined by polarization when similarly calculated. Moreover, it is possible to isolate crystalline maltose in quantity from the alcohol extract of cooked sweet potatoes. The saccharification is shown not to occur at the boiling point. The evidence that the formation of the maltose in the sweet potato is due to diastase is thus fairly conclusive. It is shown also that sugar formation in the initial stages of the action of the diastase on the starch of sweet potato tissue, while not instantaneous, is extremely rapid—e. g., slices of sweet potato dropped one by one into boiling water developed about 7 per cent of sugar calculated as maltose during the brief period when they were passing through the range at which diastase is active, this phenomenon indicating the close association of diastase with starch in the cells of the sweet potato.

The foregoing facts have many practical bearings. So far as is now known, they are unique and peculiar to the sweet potato. It is evident that the formation of maltose is of paramount importance in the production of delicious cooked sweet potatoes as we know them. The extremely rapid action of the diastase explains how it is that sweet potatoes develop a fair amount of maltose even in the tissues near the outer surfaces when quickly heated in steam or in rapidly boiling water. Differences in diastatic power between different varieties of sweet potatoes, and between sweet potatoes grown under different cultural conditions or kept under different conditions of storage, may be related to such factors as table or canning quality, and thus serve as a guide in the further development of sweet potatoes from the horticultural standpoint. It is likely, too, that the information will be of value as a guide in working out the best methods of cooking or canning sweet potatoes, especially when the highest practicable content of sugar is desired in the finished product. Again, it is known that as a consequence of the autolysis, sweet potatoes require far less malt in preparing them for sirup-making, or for fermenting and distilling, than other like materials. This fact will cheapen methods of utilizing sweet potatoes industrially as sources of sirup, alcohol, vinegar, or other products requiring the digestion of the starch through the use of malt. Thus, in sirup-making[6] a trifling amount of barley malt only, from 0.2 to 0.1 per cent of the weight of the potatoes, is required.

Since upon cooking sweet potatoes at least half, and frequently nearly all, of the starch present becomes converted into sugar, our concept of the sweet potato as a starchy food should be revised, since when consumed by man it really is saccharine rather than starchy.

It is possible too that, like barley, the sweet potato may become an important industrial source of diastase. It has already been shown[3] that raw sweet potato tissue retains its diastase during drying, and that the meal or flour produced by grinding has a diastatic power at least twice that of barley malt. In the sweet potato the diastase occurs ready formed, and does not have to be developed by the malting process.

Changes in Composition upon Cooking as in Sirup-Making

A satisfactory heat treatment for potatoes in the production of sweet potato sirup consists of cooking in live steam at atmospheric pressure for an hour and a half, allowing the condensate to run to waste during at least the first hour. In the experiment described below Southern Queen sweet potatoes, grown and stored at the Arlington Experimental Farm,[7] were used. They were washed, trimmed by cutting away all dried tissue resulting from healed bruises and withered ends of roots, and sampled by cutting sections from a number of potatoes taken at random. The sample of raw potato was ground by forcing through the die of a special sampling press of Austrian make, known as a "Herles" press.[8] The weight of trimmed potatoes was 18 kg. They were placed in a 25-gallon, steam-jacketed copper kettle and cooked for an hour and a half in a current of live steam delivered from a pipe which passed through a slot in the cover of the kettle and terminated near the bottom. During the cooking the condensed water flowed away continuously through an opening in the bottom of the kettle. After cooking the weight was 17.8 kg. The potatoes were reduced to a pulp by stirring, and a sample was taken for analysis.

The Methods of Analysis of the Association of Official Agricultural Chemists were used. Solids were determined by drying to constant weight *in vacuo* at 70° C. In determining carbohydrates, samples of 26 grams were taken. Each sample was washed into a beaker with 95 per cent alcohol and heated to boiling. It was then thrown on a suction filter, the pulp on the filter washed with alcohol and returned to the beaker. Here it was heated with a fresh portion of alcohol and the extraction process repeated several times. The extracts were combined, a little calcium carbonate added, and the whole was evaporated on the steam bath to a thin sirup. This was made up nearly to 100 cc. with water, a little lead acetate solution added, and the volume completed to 100 cc. After filtering, the excess of lead was removed by dry potassium oxalate. Reducing sugar before and after inversion with hydrochloric acid was determined by the method of Munson and Walker. Starch (together with dextrin insoluble in 95 per cent alcohol) was determined by heating the exhausted pulp with hydrochloric acid by the official method and estimating the reducing sugars formed. The results are given in Table I.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Ber.*, **23**, 1406 (1890).

[3] *J. Biol. Chem.*, **44**, 19 (1920).

[4] *Chem. Age*, **29**, 151 (1921).

[5] *U. S. Dept. Agr., Bull.* **1041** (1922).

[6] Gore, Reese, and Reed, *U. S. Dept. Agr., Bull.* **1158** (1923).

[7] Thanks are due J. H. Beattie, of the Office of Horticulture and Pomology of this department, for the generous supplies of typically cured sweet potatoes used in this work and in all the subsequent experiments.

[8] A similar press is described by Clark, This Journal, **9**, 788 (1917).

TABLE I—SUGAR FORMATION ON COOKING SWEET POTATOES

Description	Polarizations Direct ° V.	Polarizations Invert ° V.	Sucrose by Polarization %	Reducing Sugar Calcd. as Maltose %	Increase in Sugar Calculated as Maltose Determined by Reduction %	Increase in Sugar Calculated as Maltose Determined by Polarization %
Southern Queen						
Raw[a]	2.85[f]	0.00	2.15	0.23	...	...
Cooked in steam[b]	26.70[f]	23.3	2.56	11.93	11.70	11 46
Nancy Hall						
Raw	1.85[e]	0.39	4.52	0.39	...	...
Baked No. 1[c]	18.95[e]	16.45	5.06	19.69	...	...
Baked No. 2[c]	16.2[e]	14.2	4.04	17.57	...	.
Baked No. 1[d]	15.6[e]	13.5	4.16	16.19	15.8	17.2
Baked No. 2[d]	12.5[e]	11.0	3.12	13.56	13.17	13.3
Southern Queen						
Raw	2.85[f]	...	..	0.23	...	...
Whole boiled	32.8[f]	...	..	15.02	14.79	14.4
Sliced boiled	17.2[f]	...	..	7.51	7.28	6.9
Southern Queen						
Cubed $/_4$ in., raw	1.5[e]	...	..	0.34	...	...
Cubed $^3/_{16}$ in., heated 5 minutes	7.2[e]	...	..	8.32	7.98	7.13
Cubed $^3/_{16}$ in., heated 1 hour	7.05[e]	...	..	7.82	7.48	6.94
Nancy Hall						
Cubed $^1/_6$ in., raw	1.9[e]	...	..	...	...	...
Cubed $^1/_6$ in., heated 1 minute	4.5[e]	...	..	...	...	3.25
Cubed $^1/_6$ in., ground and added to boiling water	2.35[e]	...	..	...	...	0.56

[a] Solids, 33.90; starch, 22.85 per cent.
[b] Solids, 35.30; starch and dextrin, 11.77 per cent.
[c] On basis of sample as analyzed.
[d] On basis of raw weight.
[e] 10-gram sample in 100 cc.
[f] 26-gram sample in 100 cc.

A large proportion of the starch was digested, the percentage changing from 22.85 to 11.77 per cent. As a considerable proportion of dextrin was included with the starch, the actual quantity of starch was lower than indicated by analysis. The sucrose content did not change materially. A large increase in reducing sugars estimated as maltose (11.70 per cent) occurred. The increase in polarization calculated as maltose was 11.46 per cent. According to Browne,[9] the normal weight of maltose—that is, the amount of maltose which if dissolved in water and made up to 100 cc. would polarize at 100° V. in a 2-dm. tube—is 12.506 grams. Accordingly, a solution containing 1 gram of maltose in 100 cc. will polarize at 8° V. The increase in polarization observed—23.85 degrees corresponds to 2.98 grams per 100 cc., or to 2.98 × 100 divided by 26, or 11.46 per cent.

BAKING

Three large, typically shaped Nancy Hall potatoes were used. One was used for analysis in the raw state. Samples of tissue were cut from various portions, reduced to pulp in the sampling press, and sugars determined in 10-gram samples by the method described above. The other two potatoes were each fitted with a thermometer reaching to the center of the potato. The baking was done in an electric baking oven previously heated to 200° C. and maintained at this temperature during the baking. At the end of 23 minutes the temperatures recorded were 48° and 49° C., respectively. At the end of an hour the temperatures were 92° and 94° C. At the end of 77 minutes the temperatures were 99° and 100° C., when the potatoes were removed and allowed to cool. The raw potato used for analysis weighed 441 grams. The two baked potatoes weighed 450 and 396.5 grams, respectively, before baking, and 370 and 306 grams after baking and cooling. None of the tissues became carbonized. Each baked potato was ground for analysis by passing it through a meat chopper, and 10-gram samples were then taken. The sugars were extracted by the alcohol exhaustion method already described. The analyses of the baked potatoes are given both in terms of the sample as analyzed and calculated to the basis of the original weight before baking. The results are shown in Table I. The sucrose content remained substantially unchanged. A very large increase in percentage of reducing sugar reckoned as maltose occurred, amounting to 15.8 and 13.17, respectively. These values agree fairly well with the figures for the increase in the percentage of maltose determined by polarization, 17.20 and 13.3, respectively.

COOKING OF WHOLE AND SLICED SWEET POTATOES

One kilogram of pared Southern Queen potatoes, consisting of three large roots, was covered with water in a sauce pan, and heated. Nine minutes were required for the water surrounding the potatoes to come to the boiling point. They were boiled for an hour and a half, occasionally replacing the water which evaporated with fresh portions of boiling water, thus keeping them covered at all times. The water and potatoes were then mashed together to form a smooth pulp and weighed. Samples weighing 45.77 grams, corresponding to 26 grams of the original potato, were taken, and reducing sugar was determined by the methods described above.

Another lot of cooked potatoes was prepared at the same time by washing and paring three large potatoes and slicing from $^1/_8$ to $^1/_4$ inch thick in a slicing machine. One kilogram of the slices was used. They were cooked by dropping them one by one into boiling water in a sauce pan, kept boiling while the slices were being added. Four minutes were required for adding the slices. They were then boiled for an hour and a half. The cooked slices were reduced to pulp in the water in which they were cooked, weighed, sampled, and analyzed, the sample weight used being 54.34 grams, corresponding to 26 grams of the original potatoes. The results are shown in Table I.

The potatoes cooked whole contained 15.02 per cent of reducing sugar calculated as maltose, but half as much reducing sugar, 7.51 per cent, was found in the cooked sliced potato. The higher sugar content in the potatoes cooked whole can be ascribed to the fact that the potato tissues were kept for longer periods within the temperatures at which the diastase was active than in case of the sliced potato dropped into boiling water. The most striking feature, however, is the formation of so large an amount of reducing sugar during the few moments required to heat the slices as they were added to the boiling water. Thus, 7.51 per cent of reducing sugar as maltose was found in the cooked slices, but 0.23 per cent being present in the raw potato before cooking. There remained the possibility, however, that more or less sugar formation might have occurred during the boiling period. Accordingly, the experiments described below were made.

COOKING FINELY DIVIDED SWEET POTATO

Southern Queen sweet potatoes were cut into small cubes and 10-gram samples were heated for 5 and 60-minute periods in boiling water. The cubes were prepared in a slicing machine and were approximately $^3/_{16}$ inch in each dimension. Determination of the sugars present in the raw cubes was made by finely crushing 10-gram samples in a portion of water with a little alcohol, washing into a beaker, and boiling with alcohol, throwing on a suction filter and thoroughly exhausting the residue by returning it to the beaker and boiling with alcohol, again filtering, and repeating the exhaustion of the potatoes. The alcohol extracts were combined and the determination was finished as already described, the de-alcoholized solutions being diluted to 100 cc. for polarization.

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[9] "Handbook of Sugar Analysis," 1912, p. 197.

In the heating tests, 10-gram samples of the cubes were transferred to 400-cc. beakers. Each portion was then treated with 50 cc. of boiling water, set immediately on a burner and quickly heated to boiling, from 50 seconds to 1 minute being required. The boiling was then continued for 4 minutes longer in one test. In the other the total heating period was 1 hour, during which time the volume of water was kept nearly constant by the occasional addition of boiling water. At the end of the heating period, 2 volumes of 95 per cent alcohol were added to each beaker, the liquid was decanted off, and the cubes were transferred to a mortar and finely crushed. Liquid and pulp were then returned to the beaker, boiled, the liquid filtered off, and the pulp extracted twice by boiling with alcohol. The extracts were collected, evaporated, and sugars determined by methods already described. The raw potatoes contained 0.34 per cent of reducing sugar calculated as maltose, the cubes cooked for 5 minutes in boiling water contained 8.32 per cent, and the cubes cooked for 1 hour, 7.82 per cent. Thus, no sugar formation occurred at the boiling point. The experiment again demonstrated the extremely rapid saccharification which occurs when sweet potato tissue is heated through the temperature range at which the diastase acts.

INSTANTANEOUS HEATING OF SWEET POTATOES

Very small cubes, about $^1/_6$ inch in each dimension, of Nancy Hall potato were prepared. Sugar was determined in 10-gram portions of the raw cubes by crushing in a mortar in alcohol and completing the determination in the manner already described. Two heating tests were made. In one, a 10-gram portion was added to 25 cc. of boiling water contained in a beaker, set over a burner, and strongly heated. Thirty seconds were required for the resumption of boiling after the 10-gram portion had been added. The boiling was continued for 30 seconds longer, when the contents of the beaker was transferred to a mortar and 50 cc. of 95 per cent alcohol added. The cubes were then crushed, the sugars extracted and estimated, as previously described. In the other test, a portion of the fresh cubes was forced through the Herles press. Ten grams of the resulting pulp were mixed with 25 cc. of water and slowly poured with constant stirring into a beaker containing 50 cc. of actively boiling water. Two volumes of 95 per cent alcohol were then added. The sugars were then extracted and estimated in the usual manner, the polarizations only being determined.

The results are shown in Table I. During the heat treatment lasting for 1 minute, 3.2 per cent of reducing sugar calculated as maltose formed in the potato tissue. When the rate of heating to boiling was increased still further by adding the suspended pulp slowly to actively boiling water, but 0.56 per cent of reducing sugar similarly calculated was formed.

PREPARATION OF CRYSTALLINE MALTOSE

Three carefully washed and trimmed Nancy Hall sweet potatoes, weighing 1 kg., were baked for $1^1/_4$ hours in an electric baking oven at about 200° C. They were then removed and allowed to cool. They then weighed 781 grams. They were reduced to pulp and 200 grams were exhausted with four successive portions of alcohol. In making the first extraction 1 liter of 95 per cent alcohol was used. Five hundred cubic centimeters of 90 per cent alcohol were used in each of the three subsequent extractions. In making each extraction the alcohol and pulp were digested in the steam bath under a return condenser for an hour, allowed to cool, and then filtered on a Büchner funnel with suction. Each extract was evaporated to a thin sirup, transferred to a crystallizing dish, and allowed to stand with occasional stirring in a desiccator over sulfuric acid. Ten days later a very fine, white, crystalline deposit had formed in the second extract. It slowly increased in amount during the next two days, when it was filtered off with suction, and the crystals, after sucking as free from mother liquor as possible, were washed on the filter with alcohol until the washings were colorless. They were then spread out on a watch glass and dried to constant weight over sulfuric acid. The filtrate and washings were evaporated to a thin sirup and placed over sulfuric acid. During the next few days another crop of crystals gradually formed. This was recovered as described above.

Crystals began to separate from the first extract 16 days from the time it was placed in the desiccator, and slowly increased in quantity until 3 days later, when the crop was filtered off, washed, and dried as described above. The third and fourth extracts were similarly treated. The filtrates and washings from these three extracts were combined, evaporated to a thin sirup, and another crop of crystals was subsequently recovered.

The total weights of crystals obtained from the 200-gram portion of baked sweet potato and the specific rotatory power of each of the crops are given below.

DESCRIPTION	Weight G.	Specific Rotatory Power[a] [α]
First extract	9.437	130.3
Second extract	1.451	131.4
Third extract	0.831	130.2
Fourth extract	1.172	108.6
Mother liquor of second extract	0.282	128.5
Mother liquor of remaining extracts	3.999	97.9
TOTAL	17.172	

[a] Determined in a micropolariscope tube, 1 dc. long, the solutions being heated to the boiling point to destroy mutarotation and cooled before making up to the final weights. The specific rotatory power of crystalline maltose is $[\alpha]_D = 131.34$ (calculated from data given by Browne, *Loc. cit.*).

Thus, 8.59 per cent by weight of the baked sweet potato, equal to 6.71 per cent of the weight of the fresh potatoes taken, was recovered in the form of crude, crystalline maltose.

The reducing power of crystals from the first extract was determined by the Munson and Walker method. Two 200-mg. portions gave 0.2397 and 0.2401 gram of cuprous oxide, corresponding to crystalline maltose of purity 98.8 and 99.0 per cent, respectively.

The maltose was recrystallized from alcohol and compared by Edgar T. Wherry, of this bureau, with a sample of pure maltose made from starch by O. S. Keener of this bureau. The refractive indices determined by the oil immersion method and other indications were found to be identical, the indices being as follows:

α axis — 1.515 γ axis — 1.550

A. C. S. Journals Wanted

An appeal has been received for copies of the AMERICAN CHEMICAL SOCIETY'S journals from the Montanistische Hochschule, Leoben, Austria. The yearbook of this institution is offered in exchange. Subscription is said to be impossible because of the unfavorable exchange rate. If any individual wishes to help in this connection by sending his copies of the SOCIETY'S journals and at the same time receiving the above-mentioned yearbook, he should write the Austrian Consulate General, New York, N. Y.

Powdered Bordeaux Mixture[1]

By R. H. Robinson

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A method is suggested for the preparation of Bordeaux mixture in which powdered copper sulfate and hydrated lime are used in the dry form, and recommendations are made for the commercial preparation of a dry Bordeaux mixture.

THE demand for insecticides and fungicides in powder form has increased rapidly in recent years. In every respect the powder form is preferable. It may be put in convenient package; it is more economical since there is a material saving in cost of containers, transportation, and deteriorating in physical properties on storage; it reduces time and labor in the preparation of each tank of spray.

Although the powder form is preferred, it should not be used if peculiar physical properties necessary for the effectiveness of the spray are destroyed in the manufacturing process. Laboratory tests substantiated by field observations have shown that most commercial brands of Bordeaux powder are practically worthless for fungous diseases that require the toxic ingredient to adhere for several days, or for months. When Bordeaux mixture is properly made from copper sulfate and high-grade lime, a voluminous, gelatinous precipitate is formed. It does not settle rapidly, and remains evenly distributed in suspension for several hours, depending upon temperature, purity of materials used, and care exercised in its preparation. Under the microscope the precipitate is a mass of closely connected, gelatinous membranes. After several hours the membranes begin to break and the suspension gradually becomes crystalline. At this time the precipitate starts to settle rapidly. In this condition the Bordeaux is practically worthless as a fungicide, since it is easily removed from the surface upon which it is sprayed by rain, wind, or other agencies. If, however, the Bordeaux is applied when in the colloidal state, it spreads over the surface and forms an ideal, continuous film that will adhere for an indefinite length of time. Thus far no commercial Bordeaux, neither paste nor powder, that has the desirable properties of a high-grade product, has come to the writer's attention. Apparently, it is impossible to prevent the destruction of the gelatinous condition during the manufacturing process.

In an effort to prepare a very high-grade Bordeaux that would adhere for eight or ten months under Oregon climatic conditions to control anthracnose without the application of the late summer Bordeaux spray, numerous different materials were added to the spray to augment its natural adhesive properties. In the course of the work it was noticed that a good product was obtained when dry hydrated lime was sifted into a tank containing the dissolved copper sulfate to which a pound of casein spreader had been added. It was thought from this observation that a good, dry, commercial Bordeaux mixture could be prepared by using the two separate powders, into one of which had been incorporated some colloidal or protein material that would aid the formation of a gelatinous precipitate when the powders were added to the tank of water. Accordingly, a series of experiments was undertaken to ascertain the effects on the quality of the Bordeaux mixture obtained by using copper sulfate and hydrated lime that had been treated with various organic compounds.

Equivalent amounts of copper sulfate and hydrated lime were used to make a 4:4:50 Bordeaux. Since 250-cc. graduates were employed, 2.4 grams of powdered copper sulfate and 3.2 grams of hydrated lime were taken in all the combinations made. A few procedures representative of the numerous observations made are as follows:

(1) 2.4 grams copper sulfate dissolved in 250 cc. of water and 3.2 grams hydrated lime sifted in.

(2) 2.4 grams copper sulfate dissolved in 250 cc. of water and 3.2 grams hydrated lime plus 0.03 gram casein sifted in.

(3) 2.4 grams copper sulfate dissolved in 250 cc. of water and 3.2 grams hydrated lime plus 0.03 gram cane sugar sifted in.

(4) 2.4 grams copper sulfate dissolved in 250 cc. of water and 3.2 grams hydrated lime plus 0.03 gram glucose sifted in.

(5) 2.4 grams copper sulfate dissolved in 250 cc. water and 3.2 grams hydrated lime plus 0.03 gram gum arabic sifted in.

(6) 2.4 grams copper sulfate dissolved in 250 cc. of water and 3.2 grams hydrated lime plus 0.03 gram tannin sifted in.

(7) 3.2 grams hydrated lime plus 0.03 gram casein added to 350 cc. water and 2.4 grams copper sulfate sifted in.

(8) 2.4 grams copper sulfate dissolved in 250 cc. water and 0.03 gram casein plus 3.2 grams hydrated lime containing 23.8 per cent calcium carbonate sifted in.

(9) 2.4 grams copper sulfate dissolved in 250 cc. water and 0.03 gram casein plus 3.2 grams hydrated lime containing 5.0 per cent magnesium carbonate sifted in.

The temperature of the water used was 23° C. The powdered copper sulfate quickly dissolved in the water and, while stirring, the hydrated lime with organic material was sifted into the solution. Table I gives the reading on the 250-cc. graduate indicating the point to which the precipitate had settled for the stated time.

TABLE I—RATE OF SETTLING OF DIFFERENT BORDEAUX MIXTURES

No.	0.5 hr.	1 hr.	2 hrs.	3 hrs.	6 hrs.	REMARKS
1	246	240	150	Crystallized		Valueless after 3 hrs.
2	244	235	204	153	106	Good
3	242	233	213	162	115	Good
4	239	226	202	156	113	Good
5	242	210	153	121	86	Good
6	243	234	202	122	84	Good
7	111	80	59	49	44	Good
8	Did not react properly and settled to 64 immediately					
9	242	235	209	163	119	Good

With the exception of Nos. 7 and 8, all procedures gave excellent gelatinous precipitates that indicated a high-grade Bordeaux mixture. In No. 1, where no organic substance was used, a good Bordeaux was produced, but it began to crystallize after 3 hours. In the other combinations the different organic materials functioned as a stabilizer and the various precipitates retained their smooth, colloidal appearance for more than 48 hours, when they were discarded. When a poor grade of hydrated lime, having 24 per cent lime in carbonate form, was used, the chemical reaction was retarded and a granular precipitate formed that settled immediately.

In addition to the procedures given above, numerous other observations were made that warrant the following conclusions: Impurities such as iron, aluminium, magnesia, and silica if present in small amounts have no harmful effects on the quality of the precipitate. Magnesium carbonate in small amounts is beneficial. When the copper sulfate is sifted into the lime suspension, a more granular, somewhat coagulated precipitate forms, depending upon the fineness of the copper sulfate used. It is important, therefore, to sift the hydrated lime into the dilute copper sulfate solution.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

The results as a whole indicate that a high-grade Bordeaux mixture may be obtained by adding to the required amount of water, copper sulfate and subsequently hydrated lime containing a small amount of any of the organic stabilizers mentioned above. It seems preferable to recommend casein as the organic stabilizer, since the natural spreading and adhering properties of this substance have been demonstrated. It is very important that the hydrated lime be as free as possible from carbonates and coarse particles. To obtain best results about 50 per cent should pass through a 200-mesh sieve.

Recommendations for Commercial Preparations

It is advised that cartons be prepared containing the requisite amount of powdered copper sulfate and hydrated lime in separate packages. The packages of copper sulfate should be placed on top in order that it may be removed first when the carton is opened. Printed directions on cartons may read as follows:

> First, fill the spray tank with 50 gallons (for 4 pounds lime and 4 pounds of copper sulfate) of water. After starting the agitator add contents of Package A (containing copper sulfate). Then sift into the tank Package B (containing the hydrated lime plus 0.01 per cent of casein). The Bordeaux mixture is then ready for spraying.

Determination of Ash, Arsenic, Copper, and Zinc in Gelatin[1]

By **Roger M. Mehurin**

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Undesirable features of published methods for the determination of small quantities of arsenic, copper, and zinc are pointed out, and a coherent, rapid, and accurate method for the determination of ash, arsenic, copper, and zinc in gelatin is described.

Sources of possible error are enumerated so that the method will be adaptable for inexperienced analysts.

The laboratory inspection of meats, meat food products, and substances used in connection with their preparation involves the analysis of numerous samples of gelatin. In order to make certain that gelatin of suitable quality is used, samples are collected from each shipment received at any establishment at which federal meat inspection is maintained, and are submitted to the laboratory for examination. During the last year, 247 such samples were examined in the Washington Meat Inspection Laboratory. Chief among the objectionable impurities found in gelatin are arsenic, copper, and zinc. These metals are usually present in amounts not exceeding 1.4, 30, and 100 parts per million, respectively.

All the available methods for the determination of arsenic, copper, and zinc in food have been tried out, but have been found unsatisfactory when applied to the determination of these metals in large numbers of samples of gelatin. The method described in the Methods of Analysis of the Association of Official Agricultural Chemists, involving digestion with sulfuric and nitric acids, is entirely unsuitable on account of the excessive frothing, the time required for complete oxidation, and the continued exposure of the analyst to irritating fumes. The methods employing hydrolysis with hydrochloric acid have likewise proved unsatisfactory on account of difficulty in saturating with hydrogen sulfide and the subsequent filtering of large volumes of solutions which are often of such a character as to filter slowly. The determination of copper by titration with sodium thiosulfate is open to a considerable error because of the difficulty of obtaining a definite end point when small amounts are titrated. The employment of Gooch crucibles in filtering and weighing small amounts of zinc has sometimes been found to be a source of error.

The method described below has developed as a result of several years' experience in the analysis of gelatin and is free from any and all of the faults cited. While it utilizes only well-known analytical procedures, the details have been worked out and combined so as to form a coherent method by which accurate results are obtained with a minimum expenditure of time and labor. This method in substantially its present form has been in use in the meat inspection laboratories of the Bureau of Animal Industry for several years.

Arsenic

Reagents—*Dilute hydrochloric acid:* Dilute one part arsenic-free hydrochloric acid (sp. gr. 1.19) with 3 parts distilled water.

Potassium iodide solution: 600 grams per liter.

Stannous chloride solution: Dissolve 50 grams in 50 cc. arsenic-free hydrochloric acid (sp. gr. 1.19) and dilute to 200 cc. with distilled water.

Bromine water: Saturated, keep an excess of bromine in the bottle.

Lead acetate cotton: Moisten the cotton with 10 per cent lead acetate solution and dry.

Mercuric bromide paper: Prepared by dipping a small sheet of hard-surfaced drawing paper into a 5 per cent alcoholic solution of mercuric bromide, drying so as to obtain as uniform deposit as possible of the mercuric bromide, and cutting the sheet into strips 2 x 70 mm., preferably in a cutting machine prepared for this purpose.

Method—Weigh out 10 grams gelatin into a 150-cc. beaker. Add 50 cc. dilute hydrochloric acid and place on steam bath. As soon as gelatin is dissolved add 20 cc. bromine water. After digesting for one hour remove from the steam bath and cool. Make up solution to 100 cc., mix, and filter. To 20 cc. of the filtered solution add 1 cc. potassium iodide solution and 0.3 cc. stannous chloride solution. Heat on steam bath for 5 minutes, cool, and transfer to a previously prepared Gutzeit apparatus. Prepare this apparatus as follows: Add to the generator 3 grams 30-mesh, arsenic-free zinc and 20 cc. dilute hydrochloric acid; connect and allow to run for 5 minutes. Place a small amount of loosely drawn lead acetate cotton in the barrel before connecting the apparatus and a strip of mercuric bromide paper in the tube just before adding the solution. Add 0.8 cc. amyl alcohol, rinse out beaker with 3 to 5 cc. water, and add to generator. The liberated gases pass through the lead acetate cotton and over the strip of mercuric bromide paper. Allow generator to run for one hour, or longer if necessary, protecting paper from strong light. Compare with standards prepared in the same manner from arsenic-free gelatin to which known amounts of arsenic have been added. Standards should show the action of from 1 to 7 micromilligrams (0.001 to 0.007 mg.) of arsenious acid (As_2O_3).

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[1] Received March 28, 1923.

ASH

Weigh out 20 to 40 grams gelatin in a tared platinum or porcelain dish of approximately 150-cc. capacity and ash at a temperature of from 500° to 550° C. This is approximately the temperature at which the furnace presents a barely visible red when viewed through the small vent hole in the door. Samples will usually be satisfactorily ashed in from 4 to 5 hours, but no error is involved in allowing them to remain in the muffle for a longer period. It has been found convenient and economical of time to use an electric muffle furnace, placing the samples in the muffle, previously regulated so as to remain at the correct temperature, near the close of the day and allowing them to remain over night. After ashing is complete, remove to a desiccator, cool and weigh.

COPPER

REAGENTS—*Dilute hydrochloric acid:* Dilute one part (sp. gr. 1.19) with one part distilled water.

Ammonium nitrate: 100 grams per liter.

Potassium ferrocyanide: 40 grams per liter.

Standard copper solution: 0.3927 gram recrystallized copper sulfate per liter. One cc. equivalent to 0.1 mg. copper.

METHOD—Moisten the ash with a small amount of water, add approximately 5 cc. concentrated hydrochloric acid, evaporate to dryness, add 8 cc. dilute hydrochloric acid, heat to boiling, and transfer to a 50-cc. Erlenmeyer flask, using enough wash water to make the volume approximately 40 cc. Heat nearly to boiling, saturate with hydrogen sulfide, stopper tightly, and allow to stand in a warm place for one-half hour or more. Filter into a 150-cc. Erlenmeyer flask and wash promptly and thoroughly with warm 1:20 hydrochloric acid saturated with hydrogen sulfide. Transfer the paper and precipitate to a 50-cc. porcelain crucible and ignite in a muffle furnace at a temperature not exceeding that at which the gelatin was ashed. After ignition, cool, moisten ash with 1 to 2 cc. nitric acid, and evaporate to dryness on steam bath. Take up copper salts with 1 to 2 cc. nitric acid, add approximately 5 cc. water, and warm on steam bath to facilitate solution. Dilute to approximately 30 cc. and make alkaline with ammonia. Heat on steam bath, away from any hydrogen sulfide fumes, until all ammonia is expelled, occasionally diluting with water to maintain approximately the original volume. Do not evaporate to dryness. Filter into a 50-cc. graduated flask, wash out crucible with warm water, make up to mark and mix. Measure out 25 cc. into a 50-cc. Nessler tube, add 5 cc. ammonium nitrate solution, and make up to 50 cc. Add 0.2 cc. potassium ferrocyanide solution and mix. Match the color against tubes prepared in the same way from the standard copper solution. Make up standard containing 2, 3, 4, 5, and 6 cc. of standard solution equivalent to 20, 30, 40, 50, and 60 parts per million of copper if a 20-gram sample is used and one-half of solution taken. Solutions giving a stronger reaction than 6 cc. of the standard cannot be accurately compared. If a reaction stronger than that given by 6 cc. of the standard is obtained, an aliquot smaller than 25 cc. must be taken and the determination repeated.

ZINC

Boil the filtrate and washings from the hydrogen sulfide precipitation of copper until all hydrogen sulfide is removed. Add 1 cc. concentrated nitric acid and continue the boiling until the volume is reduced to approximately 25 cc. Add 10 cc. ammonium chloride (200 grams per liter), make definitely alkaline with ammonium hydrate, heat nearly to boiling, and filter into 100-cc. Erlenmeyer flask. Wash with warm, alkaline, ammonium chloride solution, containing 50 grams ammonium chloride and 25 cc. ammonium hydrate (sp. gr. 0.90) per liter. Neutralize filtrate and washings with acetic acid, add 0.5 gram sodium acetate and sufficient glacial acetic acid to make an excess of 2 cc. for each 50 cc. of solution. Warm on steam bath and saturate with hydrogen sulfide. Allow to stand in a warm place for approximately one-half hour. Filter through a small paper and wash thoroughly with warm 1:100 acetic acid saturated with hydrogen sulfide. If filtrate is turbid, return to flask, add a few drops of saturated mercuric chloride solution, shake, and filter again. Ignite in a tared platinum crucible at a dull red heat until completely ashed, then a few minutes at bright red heat. Weigh as ZnO. Weight of ZnO × 40,000 equals parts per million of zinc if a 20-gram sample has been taken.

PRECAUTIONS NECESSARY

Attention is directed to certain sources of error which must be guarded against. The gelatin must not be placed in the muffle until after the latter has reached the proper temperature, or the material will boil over the sides of the dishes before being ashed. The heat of the muffle must not reach a bright red, as loss of copper will occur in that case. Hydrochloric acid must be used in dissolving the ash. If sulfuric acid is used, a precipitate of needle-like monoclinic crystals of calcium sulfate will often form before and after the precipitation of zinc sulfide. Contamination of the zinc sulfide by traces of organic iron usually contained in the ammonium hydrate and ammonium chloride used and by traces of nickel which are sometimes found in gelatin, is prevented by the addition of an excess of acetic acid as described.

Pipet for Lactose Determination in Milk[1]

By E. G. Mahin

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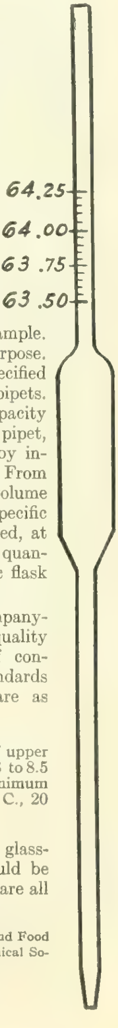
THE polariscopic determination of lactose in milk by the official method[2] involves measuring double the lactose normal weight of milk, based upon the Ventzke (or International) scale. The volume of milk to be taken varies according to the specific gravity of the milk under investigation, which means that no ordinary transfer pipet can be used for the purpose. Measuring milk samples in burets is always troublesome, especially on account of the fact that no buret is designed to deliver its entire contained quantity, and flotation of fat globules during the slow delivery gives a sample finally measured, not strictly representative of the original sample. A special pipet has been devised for this purpose. This is designed along the general lines specified by the Bureau of Standards[3] for transfer pipets. However, instead of bearing a single capacity mark, as is the case with the ordinary transfer pipet, the upper branch of the stem is graduated by intervals of 0.05 cc., from 63.50 to 64.25 cc. From the table given in the official methods the volume to be measured for a milk of predetermined specific gravity is read. This volume is then measured, at one operation, in the pipet and the entire quantity is delivered into the 102.6-cc. volumetric flask in which the proteins are to be precipitated.



The special pipet is illustrated in the accompanying figure. The general specifications as to quality of glass, finish of tip, and other matters of construction, follow those of the Bureau of Standards for transfer pipets. Other specifications are as follows:

Total length of pipet, 50 to 55 cm.; length of upper stem, 20 cm. length of graduated portion of stem, 8 to 8.5 cm.; smallest graduated interval, 0.05 cc.; minimum time of delivery for 63.5 cc. of water at 20° C., 20 seconds, maximum time, 1 minute.

Such pipets may be made by any good glassblower. Of course, all such instruments should be calibrated by the user, after their receipt, as are all volumetric instruments for work of precision.

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[1] To be presented before the Division of Agriculture and Food Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 15, 1923.

[2] Assoc. Official Agr. Chem., Methods, **1919**, 226.

[3] *Bur. Standards, Circ.* **9**.

Determination of Beta-Naphthol in Alpha-Naphthol and of Alpha-Naphthol in Beta-Naphthol[1]

By John Prochazka

Central Dyestuff & Chemical Co., Newark, N. J.

IN 1897 Liebman[2] published a method of determining small quantities of α-naphthol in β-naphthol, founded on the greater affinity of the former for diazo compounds. This was an improvement on an older method described by the same investigator in the same article, founded on the color imparted to the precipitate formed with ferric chloride and naphthol in alcoholic solution.

About the same time the author employed the same principles as Liebman in a method devised by himself and published later.[3] To his knowledge no method of determining the percentage of a small quantity of β-naphthol in α-naphthol, except the one described by Fierz,[4] has been published. A number of years ago it was found desirable to work out a method for the determination of β-naphthol in α-naphthol, in connection with the manufacture of Pure Orange I made from pure α-naphthol, the use of which as a food color was authorized by law.

The first thought was to make use of the well-known insolubility of β-naphthol azo compound in caustic soda as opposed to the solubility of the α-naphthol compounds. The chief objection to this method is the formation of a small quantity of what is presumably an ortho azo compound of α-naphthol, which also is insoluble in caustic soda. Another difficulty is the retention of a part of the α-naphthol compound in the insoluble β-naphthol compound.

Experiments were made with diazobenzene, diazoxylene, p-nitrodiazobenzene, and p-nitrodiazoxylene.

Further experiments were made based on the selective affinity of diazo compounds for α-naphthol. Contrary to Fierz,[4] diazobenzene combines, although slowly, with β-naphthol in acid—especially, acetate and acetic solution—so that any method based on the supposed inability of β-naphthol to combine must give erroneous results. Moreover, the method described is cumbersome and difficult of execution.

The same is true of a method employed in this laboratory. α-Naphthol was dissolved in grain alcohol, and combined with 50 per cent of the theoretical p-nitrodiazobenzene, the precipitate was filtered off hot and washed with hot water, and the filtrate extracted with benzene, the benzene extract evaporated, and the recovered naphthol treated the same as the original sample until the point was reached where part of the β-naphthol was coupled. The β-naphthol compound was separated from the α-naphthol in hot caustic solution, and the para red weighed, examined as to purity with the sulfuric acid color test, thus obtaining an approximate idea of the percentage of the β-naphthol.

Procedure

From this method the following very simple procedure was developed:

Dissolve 0.36 gram α-naphthol in 30 to 40 cc. grain alcohol. Cool off to below 5° C. Add gradually a solution of p-nitrodiazobenzene, of which 100 cc. are equivalent to 1 gram of nitrite. This solution may be prepared according to known methods. It should contain only a very slight excess of nitrous acid, and a not too large excess of hydrochloric acid (30 to 50 per cent of theory). If the α-naphthol is 100 per cent, 17.25 cc. diazo solution would be needed to convert it to the azo compound. If the sample is supposed to contain 10 per cent β-naphthol, add about 85 per cent of the theoretic quantity—viz., 14.6 cc. of the diazo solution—stirring carefully and keeping cold. The color begins to separate at once. It is well to wait 20 to 30 minutes, as the reaction takes time for completion. Then spot on a piece of white filter paper. If the reaction is not complete a spot of dilute caustic soda running into the first spot will produce a blue line if there is unchanged α-naphthol present. If the α-naphthol falls short of the 85 per cent diazo, the β-naphthol will combine and the mixture of the α- and β-naphthol will produce a gray line with the caustic, or the β-naphthol alone will give a red line, this red line sometimes appearing outside of the gray line. If all the diazo solution has been absorbed, the caustic soda will produce only a faint color, owing to the little azo compound dissolved in the solvent. If the β-naphthol does not show, continue adding the diazo until the para red due to the β-naphthol present begins to show in the spot test as described. If the quantity of diazo solution added is 16 cc., 16:17.25 represents the purity of the α-naphthol—viz., 92 to 93 per cent.

Procedure for Determination of α- in β-Naphthol

Dissolve 1.44 grams β-naphthol in 50 cc. grain alcohol and add 3 cc. p-nitrodiazobenzene and 0.03 gram nitrite. If the percentage is less than 0.5, all the α, and some β will be precipitated as p-nitroazobenzene compound. Let stand half an hour, then dilute with 60 cc. boiling water, filter hot through a suitable filter, and wash the precipitate with hot water. All the β-naphthol not combined passes into the filtrate, with some impure azo compound of the α-naphthol. The precipitate is washed off the filter, boiled with 50 cc. hot water containing 1 cc. 25 per cent caustic soda, filtered hot, diluted to 100 cc., and compared with a standardized solution of p-nitroazobenzene α-naphthol.

This solution is prepared as follows: 0.1 gram of the azo compound is dissolved in 25 cc. warm grain alcohol containing 1 cc. 25 per cent caustic soda and diluted to 50 cc. with hot water. The alcoholic filtrate is also made alkaline with caustic soda and compared with the standard. It is generally not as pure blue as the standard, but is included in the calculation.

Calculation—If the standard is diluted about thirty times to match its color with the solution in question, with strips of filtering paper dipped in, it would mean that 30 × 500, or 1500 cc. of it contain 0.1 gram color, and as there are only 100 cc. these would contain 0.1/15 = 0.0066 gram. 1.44 grams naphthol would yield 2.93 grams azo compound; hence, the percentage of α-naphthol would be 0.0066/2.93 = 0.23 per cent. Figured to simplest form, dividing 6.9 by dilution factor—30 in this case—gives 0.23 per cent.

If more diazo solution is added, it is impossible to extract all the alpha compound from the para red. If, however, more α-naphthol is present, more diazo should, and can, be added.

The chief objection to Liebman's method[2] is the extremely fugitive character of the blue color. In an experiment made in this laboratory according to his direction, the color faded after 20 minutes. The coloration obtained in the method here described is also fugitive, but holds out considerably longer. As the standard solution is not very stable, it was replaced by a solution of Diamine Blue 2B (benzidine tetrazotized and coupled with H acid in soda solution), the strength being adjusted to the freshly prepared standard. In diluting the standard it is well to add 1 cc. caustic to every 50 cc. of pure distilled water used.

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[1] Presented before the Division of Dye Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *J. Soc. Chem. Ind.*, **16**, 290 (1897).

[3] *Ibid.*, **16**, 894 (1897).

[4] *Farben Chemie*, **1920**, 296.

Bath Temperatures of Viscometers of the Saybolt Type[1,2]

By Winslow H. Herschel

Bureau of Standards, Washington, D. C.

Standard temperatures should be adopted for the Saybolt viscometer bath in order to get reproducible results.

Times of flow thus obtained cannot be used to calculate absolute viscosities at the nominal temperature of test, unless allowance is made for the difference between the nominal temperature of test and the average temperature of oil in the outlet tube during the run.

The variation of temperature in the oil tube during the run may be observed, in the U and F viscometer, from readings of a thermometer kept in the oil tube during the run, and the average oil tube temperature may be used in calculating correction factors for obtaining the absolute viscosity at the nominal temperature of test.

Viscosity at a given temperature is a definite physical constant of a liquid, and a viscometer may be judged either as an instrument to determine true viscosity at a known temperature, or as an instrument to obtain some measure or indication of viscosity under specified conditions. In the latter case the important consideration is whether results of different laboratories agree, but it has been found very difficult, if not impossible, to obtain adequate agreement unless instruments are so standardized as to be suitable for obtaining true viscosity at a known temperature.

Where the viscometer tube is almost completely submerged in a constant temperature bath, and there is little or no doubt that the liquid in the capillary or outlet tube is at the same temperature as the bath during the entire period of test, there is no question in regard to the proper bath temperature. There is only a question of its constancy. When, however, a part of the instrument containing the oil under test projects above the level of the bath, as in the Saybolt and Barbey viscometers, a distinction must be made between the actual and nominal temperatures of test, the former being the average temperature in the outlet tube during the timed interval. The difference between the actual and nominal temperature of test will be called the temperature error, and there is a question as to what is the proper bath temperature to reduce this temperature error to a minimum, or what correction to apply to the observed viscosity.

According to the usual directions for operating the Saybolt viscometer,[3] "The bath shall be held constant within 0.25° F. (0.14° C.) at such a temperature as will maintain the desired temperature in the standard oil tube." This might be taken to mean only that the reading of the oil tube thermometer shall be kept constant until the run is started, since it is usual practice to withdraw the thermometer before starting the run. In view of this uncertainty and the increased accuracy now demanded in technical viscometry,[4] further standardization of bath temperatures appears desirable, and this paper is offered as an aid in this direction.

At the Pittsburgh meeting of the American Chemical Society a paper was presented before the Petroleum Section by Klopsteg and Stannard on "Some Factors Affecting the Accuracy of Saybolt Viscosity Measurement and Their Control." From tests made at 210° F. with the bath temperature at 212° F., it was concluded that mechanical stirring should be used in order to get a sufficiently uniform temperature of oil in the oil tube before withdrawing the oil tube thermometer and starting the test. When tests are made at 210° F., the determination of a proper method of operation is further complicated by the "cooling error,"[5] and mainly tests at the standard temperature of 100° F. will be considered here.

The U and F Viscometer[6]

In designing the U and F viscometer shown in Fig. 1, the author had in mind an instrument which might be used to measure absolute viscosity, and which would also be in agreement with other instruments of the Saybolt type when used to measure Saybolt viscosity in seconds. The essential dimensions have therefore been chosen to conform with the Saybolt instrument.[7]

In preliminary tests[8] it was found that the temperature in the oil tube could be kept constant during the run by a proper choice of bath temperatures, but, as was found later, this method of selecting the bath temperature is not of general application, as it is not possible with very heavy oils at 100° F. nor in tests at 210° F. To keep the average temperature of the oil in the oil tube at the nominal temperature of test necessitates a variation of bath temperature which cannot be readily attained with thermostatically controlled baths. It therefore seems preferable to define Saybolt viscosity as the time of flow in seconds when the bath is kept constant at a predetermined temperature, a standard bath temperature to be agreed upon for each nominal temperature of test. Correction factors must then be used to determine absolute viscosity, when desired, from readings of Saybolt viscosity.

It is desirable, for reasons which will be discussed later, to observe the variation in the temperature of the oil in the oil tube during the run, as an aid in obtaining correction factors, and it is believed that these observations are also of value as an indication whether or not the oil under test has been sufficiently stirred and is of sufficiently uniform temperature throughout before starting the run. To obtain these readings it is necessary to leave the thermometer in the oil tube during the run, and in the U and F instrument the diameter of the oil tube has consequently been enlarged

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[1] Presented before the Division of Petroleum Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Published by permission of the Director, U. S. Bureau of Standards.

[3] *Bur. Mines, Tech. Paper* **323**, 37 (1923).

[4] Delbridge, *Proc. Am. Soc. Testing Materials*, **21**, 1100 (1921); "Lubrication," The Texas Co., February, 1922, p. 22.

[5] Herschel, *Bur. Standards, Tech. Paper* **210**, 231 (1922).

[6] U and F means Universal and Furol, and the name was chosen because this instrument, by changing the outlet tube, may be used either as a Saybolt Universal or Saybolt Furol viscometer.

[7] Am. Soc. Testing Materials, Standards, **1921**, 703.

[8] Herschel, *Bur. Standards, Tech. Paper* **210**, 235 (1922)

sufficiently to compensate for the displacement of the thermometer stem, and thus keep the average head the same as in the original Saybolt instruments. The method of supporting the thermometer from the cover of the oil tube is shown in Fig. 1.

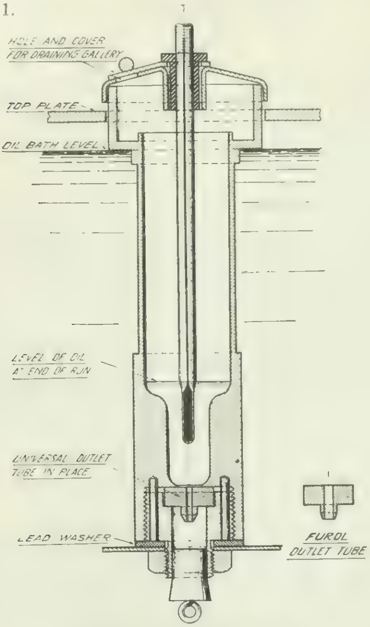
HOLE AND COVER FOR DRAINING GALLERY
TOP PLATE
OIL BATH LEVEL
LEVEL OF OIL AT END OF RUN
UNIVERSAL OUTLET TUBE IN PLACE
LEAD WASHER
FUROL OUTLET TUBE

Fig. 1—U and F Viscometer

The U and F instrument is also equipped with interchangeable, stainless steel outlet tubes, which makes it possible to use a given oil tube either as a Universal or Furol viscometer. These outlet tubes, which are flat on the ends, are easily measured by snap gages, either by the manufacturer or in the inspecting laboratory, and this is conducive to accuracy of length. It is believed that the outlet tubes will prove hard enough to resist deformation through contact with the thermometer bulb, which in time produces a burr on the top of unprotected tubes made of softer metals. Attempts have been made heretofore to protect the outlet tubes by attachments to the thermometer or to the oil tube, but such attachments present difficulties in cleaning.

Bath Temperatures

In instruments of the Saybolt type, viscosity measurements are dependent upon the temperature of the oil in the outlet tube, which in turn is determined by four factors:

1—The average temperature of oil in the oil tube during the run, Θ_w,
2—The temperature of the bath, Θ_b, assumed constant,
3—The average temperature of the room, Θ_r,
4—The time of flow, t, in seconds.

In order to secure reproducibility in determinations made in different laboratories, it is essential to standardize as many as possible of these factors. A bath temperature of 100.25° F. is now being generally used in tests at the nominal temperature of 100° F., and under these conditions the temperature of the oil in the oil tube drops during the run by an amount which varies with the time of flow and the room temperature. The average temperature of the oil in the oil tube must be determined by a series of temperature readings during the run.

The room temperature could very well be standardized at 77° F., which is the temperature most generally accepted as standard in viscometry, but if this cannot be done the variation from standard room temperature must be taken into consideration. The time of flow is not under control except in so far as it can be determined by the choice between the Universal and the Furol outlet tubes.

It had been found by tests at room temperature, where there could be no doubt about the actual temperature of test, that

$$\text{Kinematic viscosity} = \nu = A\,t - \frac{B}{t} \qquad (1)$$

where, with the Universal outlet tube, t is the viscosity, Saybolt Universal, in seconds, B is an instrumental constant sufficiently well determined as 1.80 by the standard dimensions (provided resistances to flow outside the outlet tube are negligible), and $A = 0.00220$ is another instrumental constant. The kinematic viscosity is the absolute viscosity, μ, in poises, divided by the density, ρ, in grams per cubic centimeter.

If, however, conditions are such that the temperature of oil in the outlet tube is not equal to the nominal temperature of test, and ν has been correctly determined for the nominal temperature, A will appear to have other values. For special case of a paraffin base oil of 200 seconds viscosity, with bath temperature at 100.25° F. and room temperature of 77° F., the A value appeared to be 0.00216 instead of 0.00220. It is preferable, however, to regard A as a constant for a given instrument, and independent of the conditions of test, since confusion is apt to arise when the distinction between a real and apparent A value is overlooked. On the other hand, the A value does vary with the dimensions of a particular instrument, and the value of 0.00220 applies only to instruments of strictly normal dimensions.

For any particular instrument A and B are constant, and Equation 1 will give the kinematic viscosity ν_o at the temperature Θ_o, the average temperature of the oil in the outlet tube during the run. To get ν_o, the kinematic viscosity at the nominal temperature of test Θ, a correction factor must be used somewhat as follows.

$$\nu_\Theta = \left(A\,t - \frac{B}{t}\right)\left[1 - \frac{d\,\nu}{\nu\,d\,\Theta}\,(\Theta - \Theta_o)\right] \qquad (2)$$

Equation 2 might be used to determine the temperature error, $\Theta - \Theta_o$, when ν_Θ is known, since $\frac{d\,\nu}{d\,\Theta}$, the rate of change of kinematic viscosity with the temperature, may be readily determined with sufficient accuracy. However, when ν_Θ is unknown, and it is desired to correct the value obtained from Equation 1, it is more convenient to omit from the equation Θ_o, which could only be obtained with considerable difficulty from a series of thermocouple readings. On the other hand, if the correction is applied to Equation 1 by the equation

$$\nu_\Theta = \left(A\,t - \frac{B}{t}\right)\left[1 - \frac{d\,\nu}{\nu\,d\,\Theta}\left(\Theta - \Theta_w + C\,[\Theta - \Theta_r]\right)\right] \qquad (3)$$

all the temperatures involved may be obtained from thermometer readings.

Information is not yet available for determining C, which, for approximate purposes, it may prove possible to regard as a constant. More accurately, C is a function of $\Theta - \Theta_r$, Θ_b, and the time of flow. When $\Theta = \Theta_r = \Theta_o$, the true value of ν_Θ may be obtained from Equation 1, since $\nu_\Theta = \nu_o$, but in other cases a correction factor must be applied which, for a given nominal temperature of test and temperature of bath, will vary with the room temperature, the time of flow, and the rate of change of viscosity of the oil with the temperature.

Measurement of the Relative Absorption Efficiencies of Gas-Absorbent Oils[1,2]

By Robert E. Wilson and Harold S. Davis

Massachusetts Institute of Technology and Arthur D. Little, Inc., Cambridge, Mass.

The relative absorption efficiencies for benzene of eight gas-absorbent oils were measured by two vapor tension methods developed independently by the writers. The results show that the seven petroleum distillates, which varied considerably in boiling range and method of production, were strikingly similar in the volume of benzene which could be absorbed by a given volume of the oil under specified conditions. The differences in molecular weight of the oils should have produced variations in absorption efficiencies if Raoult's law held, but, strangely enough, these differences were just about counterbalanced by he deviations from Raoult's law. The coal-tar distillate was found to be a somewhat better absorbent, but certain other properties constitute serious objections to its use in most commercial installations.

In the light of the results, it does not appear necessary to prescribe any absorption or vapor pressure test for gas-absorbent oils of the ordinary range of compositions.

The molecular weights, specific gravities, and boiling points of the various oils are given.

IT IS well recognized that there is a need for some reliable method of testing the absorbing capacity of gas-absorbent oils, for the recovery of "light oil" from gas, and for some information as to the desirability of including such a test in specifications. The writers in coöperation with Subcommittee II of Committee D-2 of the American Society for Testing Materials have applied their respective methods of measuring vapor pressures to this problem. Work by the two methods was carried on quite independently, and the results were compared upon its completion. However, the fundamental data involved were so similar that it seemed desirable to combine the results of the two sets of experiments into a single paper.

Oils Used and Molecular Weight Data

At the request of the committee, seven samples of gas-absorbent oil[3] were prepared by the Atlantic Refining Company to meet the following specifications:

1—A straight-run, midcontinent distillate, over point about 450° F., 80 per cent distilling below 680° F.

2—Representing approximately one-half Sample 1 of low boiling point.

3—Representing approximately one-half Sample 1 of high boiling point.

4—Oil of approximately the same distillation ranges as Sample 2 but acid-treated.

5—Oil of approximately the same distillation ranges as Sample 3 but acid-treated.

6—Highly cracked, midcontinent distillate of about the same distillation ranges as Sample 2.

7—Highly cracked, midcontinent distillate of about the same distillation ranges as Sample 3.

In addition to these seven, the writers desired to test a coal-tar oil[4] similar to those frequently used in England for benzene recovery.

Since absorption efficiency might be expected to vary inversely with the molecular weight of the oil[5] (if Raoult's law held), it seemed desirable to make careful determinations of this constant. Most of this work was done by F. J. Guerin at the Massachusetts Institute of Technology, by the methods described in detail in the previous article.[6] The results, together with other significant data kindly supplied by T. G. Delbridge, of the Atlantic Refining Company, for the first seven oils, are given in Table I. Plots of the molecular weight data are given in Figs. 1 to 3, inclusive.

The molecular weight determinations were all made without any knowledge of any other properties of the oils, but when the data were compared with the specifications, the consistency of the results was quite gratifying. Thus it appears that:

(*a*) The higher boiling cuts had molecular weights about forty points higher than the corresponding lower boiling cuts.

(*b*) For a given boiling range there is very little difference between the molecular weights of the cracked and uncracked products.

(*c*) Acid treating reduces the average molecular weight of the oils from eight to ten points. Since the loss on treatment is reported by Dr. Delbridge as 1 to 2 per cent, it would appear that the average molecular weight of the material removed in acid treatment was over 500; possibly much of it was really colloidal.

Table I Properties of Gas-Absorbent Oils Tested

No.	Gravity A. P. I.	Sp. Gr.	Saybolt Viscosity at 70° F.	Initial Boiling Point ° F.	50 Per cent Point ° F.	Dry Point	Mol. Wt.
1	36.8	0.841	46	449	546	760	228
2	38.6	0.832	40	426	504	666	214
3	34.8	0.851	56	497	588	776	253
4	38.6	0.832	41	432	504	668	204
5	35.0	0.850	57	502	588	774	245
6	34.4	0.853	47	464	567	680	218
7	33.4	0.858	54	514	590	708	250
8	...	1.10	180	455	620	796	167

Methods for Measuring Absorbing Capacity

The two methods employed were similar in that they measured the vapor tensions of dilute solutions of benzene of definite concentration in the various gas-absorbent oils, the better absorbers giving the lower vapor tensions.

In using the Davis method, described in detail in the subsequent article,[7] solutions containing four parts by volume of benzene in 100 parts by volume of the absorbent oils were made up by measurement of definite quantities of the liquids from standardized, graduated pipets (2 cc. and 50 cc.).

To measure the vapor tension of benzene from each of the resulting solutions, 2.3 cc. (1 per cent of the volume of the flask of the apparatus) were measured into one of the small glass containers. The upper stem of the container was then drawn out to a fine capillary, which was cut off to about 2 cm., but not sealed.

Freshly distilled, C. P. benzene was used. The greater part came over within less than 0.5° C.

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[1] Published as a joint contribution from the Research Laboratory of Applied Chemistry of Massachusetts Institute of Technology (Contribution No. 67) and from the laboratories of Arthur D. Little, Inc.

[2] Presented before the Division of Petroleum Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[3] These oils were obtained through the courtesy of C. A. Lunn, chairman of Subcommittee II on Gas-Absorbent Oils of the American Society for Testing Materials.

[4] Obtained through the courtesy of The Barrett Company.

[5] This Journal, **10**, 718 (1918).

[6] Wilson and Wylde, This Journal, **15**, 801 (1923).

[7] Davis and Davis, to appear in October issue of This Journal.

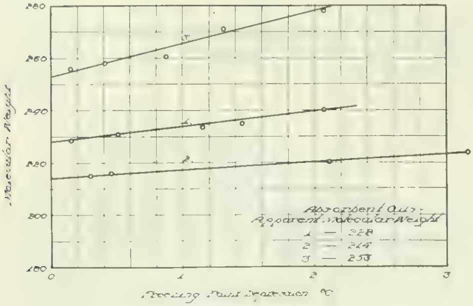

FIG. 1

To illustrate the methods of calculation and correction employed, full details are given below for the first test on absorbent oil No. 1.

Time Min.	Procedure	Pressure Mm. of Oil[a]
0	Put apparatus in bath, closed stopcocks	
3		0.0
10		−13.4
20		−13.8
25		−13.9
30		−13.9
5	Broke container inside flask	−13.9
0		61.3
10		84.0
15		93.1
20		97.2
25		101.0
30		102.5
35		103.9
40		103.9

Total pressure developed (uncorrected) = 117.8
Temperature of bath = 25° C.
Barometer pressure = 76.7 cm. mercury

[a] Gas-absorbent oil No. 1 was used as the manometer liquid in all tests.

This result must be corrected for two factors.

(*a*) The changes in the volumes of the two flasks of the apparatus due to the movement of the manometer liquid. This was calculated from the following data:

Volume of 1-cm. length of manometer tube = 0.052 cc.
Average volume of the two flasks = 234 cc.
Barometer pressure = 767 mm. mercury

The change in volume of the air in each flask for a change in the levels of the manometer liquid of 1 cm. = $\frac{0.052}{2}$ cc., corresponding to a change in pressure of $\frac{0.052 \times 767}{2 \times 234} = 0.085$ mm. of mercury, so that the total correction due to the changes in pressure in both flasks is 0.17 mm. of mercury.

Now, 1 cm. of the oil used for manometer liquid (sp. gr. = 0.833) = 0.0614 cm. of mercury. Consequently, the observed reading must be increased by $\frac{0.17 \times 100}{0.614} = 27.5$ per cent to correct for this factor.

(*b*) The change in concentration of the solution due to the partial evaporation of benzene into the flask:

Let v = volume of flask in cubic centimeters
w = grams of benzene in the solution in the container
P = benzene pressure developed in millimeters of mercury

Then at 25° C. the percentage of benzene which evaporates into the flask is $\frac{0.00042\,P\,v}{W}$.

In the case of the test above this correction is 13.9 per cent, so that the total correction factor by which the readings should be multiplied is 1.275 × 1.139 = 1.45.

The corrected vapor tension of a 4 per cent solution of benzene in this absorbent oil is therefore 170.8 mm. The detailed results on all the oils are discussed in a subsequent section.

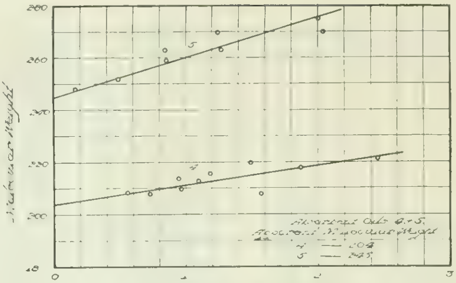

FIG. 2

The Wilson-Wylde method and calculations were described in detail in the preceding article.[6] Most of the oils were tested with only one concentration of benzene—approximately 5 per cent by weight (the precise concentrations differed slightly and were of course taken into account in plotting the results). Measurements were made at a series of temperatures between 20° and 120° C. The temperature coefficients were in all cases small and similar to those for gas-absorbent oils Nos. 2 and 3, for which the complete curves are given in Fig. 5. Since the 60° C. values are considered the most reliable, they were used for comparative purposes.

DISCUSSION OF RESULTS

Unfortunately, since the problem was originally attacked independently by the two laboratories, the concentrations used in the two cases were appreciably different, making direct comparison impossible. Furthermore, the Davis measurements were all at 25° C., while the Wilson-Wylde results were most reliable at 60° C. It therefore seemed best to compare the results graphically in order to study the deviations from Raoult's law as shown by the two sets of observations. The observed vapor tensions were therefore calculated as percentages of the saturation tensions at the same temperature and plotted against the molecular fraction of benzene in the solution, as shown in Fig. 4. The lines are drawn straight through the origin and the observed points, as demanded by Henry's law, which should hold fairly accurately in this region. By comparing the intersection of the two sets of lines with the 12 per cent saturation lines at which they end, it is possible to compare closely the results obtained by the two methods.

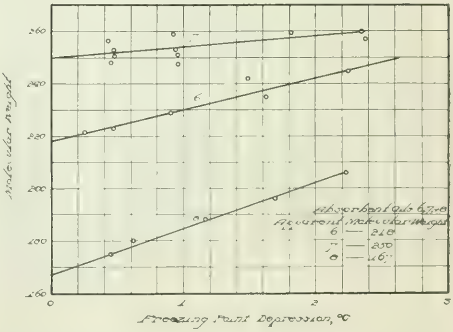

FIG. 3

The consistency of the results is on the whole quite satisfactory, considering the large corrections which must be

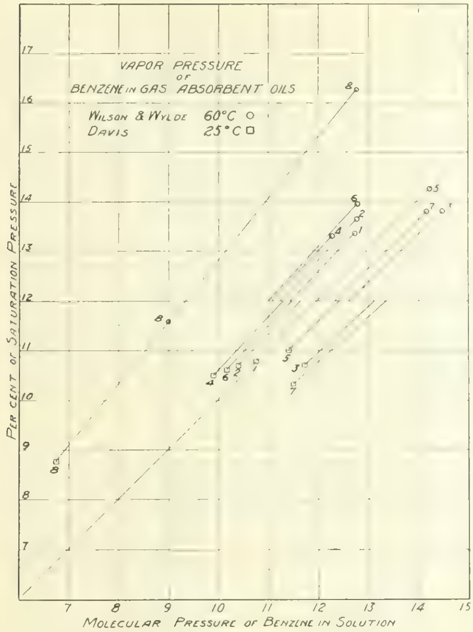

FIG. 4

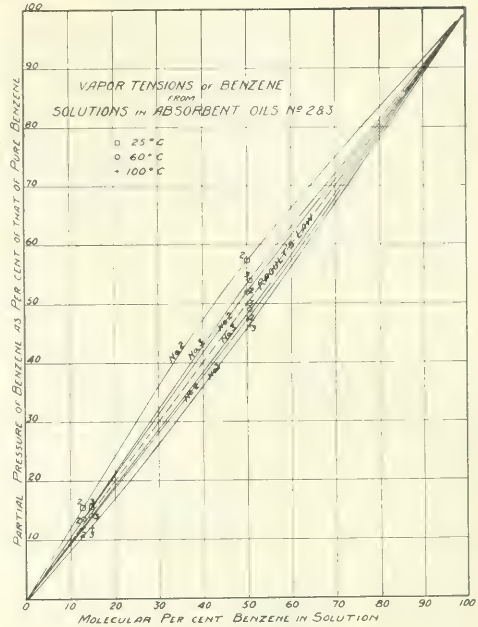

FIG. 5

applied to the first method and the manipulative difficulties of the second. In both sets of results, oils Nos. 2, 4, and 6 (the three low boiling ones) are grouped together with deviations slightly above Raoult's law, while the three high boiling cuts, Nos. 3, 5, and 7, are similarly grouped with negative deviations, oil No. 1 occupying an intermediate position. Oil No. 8, the coal-tar distillate, gave much higher results in both sets of experiments.

Even the relative positions of the oils in the two groups are fairly consistent, but the variations between the members of the groups are so small that this must be considered as more or less accidental (note that the figure is drawn on a very large scale).

As a whole, the Davis results are 2 to 3 per cent lower than those of Wilson and Wylde, which is not surprising under the circumstances. The ratio of liquid volume to air space is about four hundred times greater in the latter than in the former case, so the tendency is to get high results by the latter method and low ones by the former. The average should be fairly near the truth. The discrepancy would be a little greater if the less reliable 25° C. values of Wilson and Wylde were used.

At any rate, there can be no serious doubt as to the reliability of both methods within a very few per cent, and the comparative results between different oils by the same method are probably good within 1 per cent if proper precautions are taken.

Since the method of plotting in Fig. 4 placed the seven oils in two groups as far as deviation from Raoult's law is concerned, it might be expected that this division signifies real differences in absorption efficiencies. Surprisingly enough, however, the magnitude and direction of these deviations are very nearly such as to counterbalance the differences which would be caused by the variations in the molecular weight if Raoult's law held.

In other words, the oils which would be expected to give better absorption because of lower molecular weights deviate from the predictions of Raoult's law just about enough to nullify this apparent advantage. As a result the percentage by volume of benzene absorbed by the different oils under given conditions is substantially the same for all, as indicated by the following tabulation of results:

RELATIVE AMOUNTS OF BENZENE ABSORBED FROM AIR 12 PER CENT SATURATED WITH BENZENE VAPOR BY DIFFERENT GAS-ABSORBENT OILS

			MOLAR PER CENT ABSORBED			PER CENT	
SAMPLE	Molecular Weight	Sp. Gr. 60° F.	Wilson and Wylde	Davis	Average	By Weight	By Volume
1	228	0.841	11.42	11.93	11.68	4.33	4.15
2	214	0.832	11.22	11.62	11.42	4.48	4.26
4	204	0.832	11.09	11.29	11.19	4.60	4.38
6	218	0.853	11.00	11.46	11.23	4.32	4.18
Average 2, 4, 6	212	0.839	11.10	11.46	11.28	4.47	4.27
3	253	0.851	12.58	13.06	12.82	4.33	4.22
5	245	0.850	12.00	12.40	12.20	4.23	4.13
7	250	0.858	12.30	13.37	12.83	4.39	4.32
Average 3, 5, 7	249	0.853	12.29	12.94	12.61	4.32	4.22
Average of all	230	0.845	11.66	12.16	11.91	4.38	4.26
8	167	1.10	9.32	9.32	9.32	4.57	5.64

While there are certain variations in the last column for the first seven oils, they are barely beyond the experimental error, are not consistent with any of the properties of the oils, and are quite without significance commercially—a difference of 1° to 2° C. in temperature making more difference in the absorption capacity in any one than any of the variations observed between the oils themselves. Since there is no consistent difference in the percentages absorbed by volume, the slight advantage of the lighter oils shown in the weight per cent column is due to their lower specific gravities.

Gas-absorbent oil No. 8 stands out from the petroleum products in all the tests. Its deviation from Raoult's law is very large and positive, as might be expected from the chemical dissimilarity between an oxygen compound and a hydrocarbon. Nevertheless, this apparent disadvantage is more than overcome by the very low molecular weight of the coal-tar oil, and the percentage of benzene absorbed by weight is slightly higher than that taken up by the petroleum oils under similar conditions. This oil is so dense, however, that the volume percentage held is considerably greater. Its excessively high viscosity (especially when cold), greater cost, and difficulty of handling in steam distillation would almost certainly rule it out under present conditions in this country, although the English claims of greater absorption efficiency appear to be justified. At the same time, the possibility of using coal-tar products under special conditions should not be overlooked.

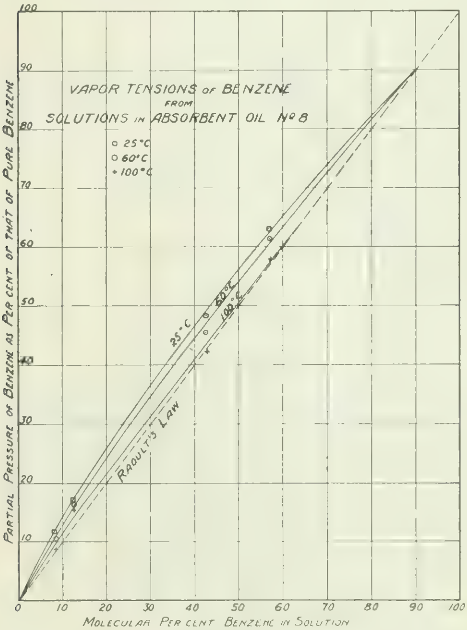

FIG 6

In order to study the deviations from Raoult's law over the whole range of concentrations, more observations were made by Wilson and Wylde on the three representative absorbent oils. The results on Nos. 2 and 3 are shown in Fig. 5 and those on No. 8 in Fig. 6. The curves indicate that the deviations from Raoult's law are consistent over the whole range of concentrations. They also bring out the effect of temperature on the relative vapor tensions of the different solutions, higher temperatures giving slightly lower relative vapor tensions.

A comparison of the benzene absorption capacities on a weight basis, of gas-absorbent oils Nos. 2, 3, and 8, is shown in Fig. 18 of the previous article. Throughout the whole range, the similarity between all the hydrocarbon oils is indeed striking, considering the wide variations in molecular weight, etc.

RECOMMENDATIONS REGARDING AN ABSORPTION TEST FOR GAS-ABSORBENT OILS

After a careful comparative study of these two methods and the results obtained, the writers agree to the following conclusions regarding the problem of testing gas-absorbent oils:

1—Cost considerations and certain necessary physical properties—especially viscosity at low temperatures and initial boiling point—practically limit the choice of gas-absorbent oils for benzene in this country to a comparatively narrow range of mineral-oil fractions. All the samples tested appear to have absorptive capacities so nearly identical that the addition of a rather complicated absorption test to the other physical tests required does not appear to be justified.

2—While the method used for molecular weight determination is quite satisfactory for the purpose, the result is not directly significant as a measure of the absorptive capacity of the oil, and hence should not be made the basis for any requirement.

3—For research purposes, involving the study of a wider range of absorbent oils for benzene or absorbents for other volatile solvents, either of the two vapor tension methods referred to, with the specified precautions, will give satisfactory results. For the comparison of absorptive capacities at a single moderate temperature, the Davis method is undoubtedly simpler, but if information is desired at a number of different temperatures, and especially at temperatures above 40° C., the Wilson-Wylde method is more reliable and requires less time.

Motion Picture Films

The International Committee of Young Men's Christian Associations, New York, N. Y., has secured a number of new films since the publication of the list in the March issue of THIS JOURNAL. Among these are the following:

1224	Hemp to Hawsers	Wall Rope Company
1225	From Logs to Lumber	Southern Pine Association
1228	The Spirit of the Birch	Sidway Mercantile Company
1229	Shoeing the Horse of Progress	Kelly-Springfield Tire Company
1231	Among the Tire Builders	
1234	The Rice Industry	Rice Millers of America
1235	Summer in Winter	Monitor Stove Company
1236	Story of a Watch	Illinois Watch Company
1237	Story of Virgin Wool	Strong and Hewat
1239	The Making of a Book	Doubleday, Page & Company
1240	The Birth of a Hat	J. B. Stetson & Company
1241	Story of Compressed Air	Compressed Air Society
1242	History of the Telephone	American Telephone & Telegraph Company
1243	From Calves to Kiddies	McElroy-Sloan Shoe Company
1244	The Danger That Never Sleeps	National Board of Fire Underwriters
1252	The Valley of Fair Play	Endicott-Johnson Corporation
1253	Tanning	
1254	Shoemaking	
1255	The Romance of an American Soft Drink	Chas. F. Hires Company
1257	Ore Pits to Billets	U. S. Steel Corporation
1258	Rails and Plates	
1259	Wire and Wire Products	
1260	Pipes and Tubes	
1261	Tin Plate	
1262	The Human Side of Steel Making	
1263	A Miracle in Typewriters	Shipman Ward Manufacturing Company
1266	Sanitation at Home and on the Farm	Phinotas Chemical Company
1269	King Cotton	Alabama Power Company
1270	Electricity at Work	
1271	Minerals and Metals	
1272	Water by Wire	Duro Pump & Machinery Corporation
1273	Dates from the Garden of Eden	Hills Brothers Company
1092	Inside Out (Digestion)	Standard Oil Company
1275	Milady Beautiful	National Hair Goods Company
1150	Where Dollars Have Sense	H. C. Boback Company
1004	A Pullman Travelog	Pullman Company
1001	Yours to Command	National Electric Light Association
1012	The Modern Goliath	Bucyrus Company
1014	Meat for Health	Institute of American Meat Packers
1036	Story of the V-Type, 8-Cylinder Motor	Cadillac Motor Car Company
1041	A Blessing Born in the Agony of War	Zonite Products Corporation
1061	Heath o' the Wheat	C. F. Mueller Company

The Quantitative Determination of Sulfur Forms in Coke[1,2]

By Alfred R. Powell

Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

Methods have been developed for the quantitative determination of the four forms of sulfur which exist in coke. These methods have proved to be accurate, and can be applied without the use of elaborate apparatus.

IN another paper the writer[3] has described an investigation in which the nature of the sulfur present in coke was determined. As the coke existed in the oven, two forms of sulfur were present—namely, ferrous sulfide and sulfur held in the carbon apparently in the form of a solid solution. During the quenching of the coke, however, oxidation takes place, so that a portion of the ferrous sulfide is oxidized to iron oxide and free sulfur, a much smaller part of the ferrous sulfide is oxidized to sulfate, and another part of the ferrous sulfide remains unchanged. Therefore, the finished coke will contain sulfur in four forms: (1) ferrous sulfide, (2) sulfates, (3) free sulfur adsorbed on the surface of the coke, and (4) sulfur held in solid solution in the carbon.

Coke which has been made by fast heating, such as that made in small quantities in the laboratory or made in small gas retorts, does not quite conform to these conditions, which apply to coke made by the ordinary process in the by-product oven or in the beehive oven. Coke made by fast heating contains sulfur in three forms before removal from the retort, instead of the two mentioned for the ordinary oven coke. The third form is adsorbed free sulfur, which seems to be driven to the surface of the coke by the fast heating, rather than entering the carbon in solution. When this coke is quenched, as a result of the consequent oxidation it contains the same four forms as the oven coke.

The methods by means of which the nature of the coke sulfur was investigated, and which have been described in the paper referred to, gave a method for the quantitative determination of the sulfur forms in coke, but it involved the use of a complicated apparatus, accurate temperature control, a long series of titrations, and many other disadvantages. It was entirely unsuitable for the analysis of the sulfur forms in coke, although it proved to be invaluable in determining what was the character of those sulfur forms. A quick, accurate, and convenient method was therefore sought, by means of which quantitative analyses could be made of the four sulfur forms in coke samples.

EXPERIMENTAL

FERROUS SULFIDE—With the exception of very small quantities of calcium and magnesium sulfides, ferrous sulfide is the only metallic sulfide occurring in coke. The determination of this substance, therefore, amounts to a determination of the metallic sulfide content, which is very easily performed. The method which the writer has used for the determination of ferrous sulfide in coke has been described in another paper,[4] so that no experimental work was necessary.

SULFATE—The determination of the sulfate content of coke has been described in the paper just referred to.

FREE SULFUR—The determination of the free sulfur held on the surfaces of the coke in an adsorbed condition required considerable experimental work in its development. At the outset it was realized that no direct method could be used, since solvents will not extract the adsorbed free sulfur from the coke quantitatively, heat will not drive out this form of sulfur to any extent, and any method of attack must involve chemical combination of the sulfur.

As stated before, the previous investigation of the forms of sulfur in coke had produced a method by means of which the quantity of the various sulfur forms present could be determined. The examination of the coke involved a phase rule study of the coke sulfur. With the coke at a constant temperature, the pressure of free-sulfur vapor over the coke was measured. The sulfur was then removed from the coke in small successive amounts and the vapor pressure of sulfur was redetermined after each removal. Thus, a curve was obtained which expressed the relationship between the amount of sulfur in the coke and the pressure of free-sulfur vapor over the coke, the temperature being constant. Phase rule deductions, then, give us a method for determining how much of the sulfur in the coke is ferrous sulfide and how much is in the solid-solution form. The other two forms of coke sulfur were not present under these conditions, since the method of measuring the vapor pressure of the sulfur depended on the passage of hydrogen over the coke, and the conditions were therefore strongly reducing. However, this previous investigation had shown that the free sulfur and the sulfates in coke had resulted from the oxidation of some of the ferrous sulfide, and that the sum of the ferrous sulfide, the free sulfur, and the sulfates in the coke which had been subjected to oxidation, was equal to the original content of ferrous sulfide in the coke under reducing conditions. Therefore, since the ferrous sulfide and sulfates could be determined in the coke by known methods, and since the sum of the ferrous sulfide, the sulfates, and the free sulfur had been determined by the phase rule study, the free-sulfur content of the coke was known.

SOLID-SOLUTION SULFUR—Since this was the only form of sulfur in the coke for which an analytical method had not been worked out, it was very readily determined by difference from the total sulfur.

The testing of samples for a quick and accurate method of analysis could therefore be carried on with the use of coke samples of known free-sulfur content. Several of these samples were available, and were used in the present investigation.

ROASTING METHOD

The first method investigated was the roasting of the coke at such a temperature that the ferrous sulfide and adsorbed free sulfur would evolve their sulfur as sulfur dioxide, and be determined as such. Provided that this treatment were carried on under such conditions that the coke itself would not be oxidized, the sulfur held in solid solution by the carbon would not be affected, since it is extremely stable. The sulfates, of course, would remain in the coke. Since the ferrous sulfide content of the coke would have been determined already, it would be possible to calculate the adsorbed free sulfur by difference.

Trials at several different temperatures showed that 500° C. was the best temperature for the oxidation of the sulfur without causing any measurable loss of coke. The powdered coke was placed in a boat, and this was put in a tube kept in a furnace at 500° C. Air was passed over slowly for about a half hour. For the purpose of absorbing the sulfur dioxide, the air passing out to the tube was bubbled through sodium hydroxide solution. This solution was later acidified and titrated with iodine.

The results from this roasting method were very unsatisfactory. Analysis of the residual coke showed that the ferrous sulfide had completely disappeared. However, the results were invariably low, showing that the free sulfur and the ferrous sulfide had not oxidized quantitatively to sulfur

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[1] Received March 15, 1923. Presented before the Section of Gas and Fuel Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] *J. Am. Chem. Soc.*, **45**, 1 (1923).

[4] THIS JOURNAL, **12**, 1069 (1920).

dioxide. Indications pointed to the fact that some of the sulfur was oxidized to sulfur trioxide, as shown by the presence of a faint mist in the outlet air and an increase in the sulfate content of the coke. The low-temperature roasting method for the free-sulfur content of coke was therefore abandoned.

Reduction Method

The next method tried was a reduction method. Since the free sulfur and the sulfates in the coke are formed by oxidation during the quenching of the coke, it was thought that the reduction of the coke would re-convert the free sulfur and the sulfates into ferrous sulfide. The ferrous sulfide could then be determined, and by subtracting the ferrous sulfide and sulfates in the original coke the free-sulfur content of the original coke would be known.

The reduction was carried out by placing a weighed amount of the powdered coke in a boat, inserting this boat in a tube combustion furnace, and finally reducing the coke at a red heat with hydrogen. The tube was first rinsed out with hydrogen to eliminate all air, then the outlet was closed and a very slight pressure of hydrogen was maintained in the tube to insure a thoroughly reducing atmosphere at all times. After the tube had reached a red heat, the heating current was turned off and the tube was allowed to cool, the atmosphere of hydrogen being maintained, of course, until the tube was entirely cool. The ferrous sulfide was then determined in the coke in the usual manner. The following table gives the results from a variety of cokes:

	Percentage of Sulfur in Coke					
Class of Coke	Total	FeS (Phase Rule Curve)	FeS (After Reduction by H_2)	FeS (Original Coke)	SO_4 (Original Coke)	Free S (Original Coke)
Gas-house	2.04	1.02	1.00	0.64	0.00	0.36
Illinois by-product	1.31	0.45	0.47	0.26	0.02	0.19
Pennsylvania by-product	1.10	0.40	0.41	0.21	0.00	0.20
Pennsylvania by-product	0.95	0.25	0.27	0.02	0.00	0.25
Beehive	0.82	0.26	0.26	0.11	0.00	0.15
Vertical retort	3.20	....	1.30	0.58	0.10	0.62

Comparison of the figures in the second and third columns gives an indication of the accuracy of the method. The second column shows the percentage of sulfur as ferrous sulfide in the coke under reducing conditions, obtained by measuring the ferrous sulfide line of the phase rule curve, which has been referred to earlier. This is an absolute measure of the ferrous sulfide content under the given conditions, and serves as the standard by which the accuracy of the method may be judged. The third column gives the ferrous sulfide content obtained by chemical analysis after the coke had been reduced; the next two columns give the ferrous sulfide and sulfates in the original coke, as determined by analysis; while the final column gives the free-sulfur content of the original coke, calculated by subtracting the ferrous sulfide and the sulfate sulfur of the original coke from the ferrous sulfide sulfur after reduction of the coke.

These results show that the method is reliable and can be depended upon for the determination of the free-sulfur content of coke. This method has been used in several investigations since its development, and the whole trend of the results has shown that it is a convenient and accurate analytical process.

It has been mentioned that coke made by fast heating contains free adsorbed sulfur even in the reduced state. Cokes of this type are seldom encountered in industrial practice, but are confined mainly to cokes made in small batches in the laboratory. In one of our investigations, however, a gas-retort coke was found which gave very irregular results when analyzed by the foregoing method for free sulfur. Investigation showed that this coke contained free sulfur in the reduced state—in other words, more free sulfur than the iron present in the coke could combine with to form ferrous sulfide.

Special treatment of this coke during the reduction with hydrogen was therefore necessary in order to convert all the free sulfur into sulfide sulfur. This was very readily accomplished by mixing a small amount of calcium oxide with the coke before introduction into the reducing tube, thus furnishing the necessary material to convert all the free sulfur into sulfide sulfur. For the purpose of the analysis it did not matter into what sulfide the free sulfur was converted, because the subsequent treatment with hydrochloric acid released the sulfur as hydrogen sulfide. The results obtained with this modification were very consistent and satisfactory.

Complete Analysis of Sulfur Forms in Coke

After the total sulfur has been determined by any one of several well-known methods, two samples of the coke, which has been crushed to at least 35-mesh size, are weighed out. These should preferably be 2-gram samples, although in the case of high-sulfur coke 1 gram may be sufficient.

One of these samples is placed in a 200-cc. Erlenmeyer flask, and 25 cc. of water are added. This flask is connected with a test tube containing 10 cc. of ammoniacal cadmium chloride solution, in such a manner that any gas coming out of the flask will bubble through the cadmium chloride solution. Hydrogen is then passed through the flask in order to sweep out any air, and then 25 cc. of concentrated hydrochloric acid are added to the flask, which is gently heated until all the hydrogen sulfide has passed over into the adsorption tube and is then disconnected. The solution with the yellow precipitate in the tube is washed out, diluted with 300 cc. of water, acidified, and then titrated with standard iodine solution. The sulfur so determined represents the ferrous sulfide content of the original coke.

The contents of the Erlenmeyer flask are filtered, the filtrate is made slightly ammoniacal, and then brought back to a slightly acid condition with a few drops of hydrochloric acid. The sulfate is precipitated by barium chloride in the usual manner, and the subsequent analysis indicates the sulfate content of the original coke. This is always very small and in a great many cases is a mere trace. Separation of the iron from the solution before the precipitation of the barium sulfate is not necessary.

The other sample of coke is placed in a small porcelain boat, and this is inserted into a silica tube in a heating furnace. While the furnace is still cold, the tube is thoroughly swept with hydrogen and then closed at the outlet end. A slight pressure of hydrogen is kept in the tube, most conveniently by a T connection, which releases the excess hydrogen from the cylinder through a tube leading down through a few inches of water. The furnace is heated to a full red heat, and then the tube is allowed to cool to not more than 100° C. The boat is removed from the tube, and the contents are placed in an Erlenmeyer flask and treated in exactly the same manner as was the sample for the ferrous sulfide determination. The sulfur so determined represents the sum of the ferrous sulfide, sulfate, and free sulfur. The free-sulfur content of the original coke can be calculated by subtracting from this figure the ferrous sulfide and sulfate sulfur, which have been previously determined. In the operation of the reduction furnace used for this determination due care should be taken to prevent any hydrogen explosion.

In case the coke under examination is suspected of containing free sulfur above the amount with which the iron can combine, a duplicate run should be made for free sulfur. In this case about 0.2 gram of pure calcium oxide should be mixed with the powdered coke before it is placed in the combustion boat. Any difference between this determination and the one made in the normal manner would show the amount of free sulfur in the coke above the amount necessary to combine with the iron. Such cases will arise only where the coke has been made by fast heating, such as coke made in the laboratory or in small retorts with very hot walls. Of course, if no differentiation is desired between the free sulfur which will combine with the iron of the coke and any excess free sulfur which may be present, the lime may be added in all cases. However, it is desirable to determine these separately, since free sulfur above that which will combine with the iron of the coke will have a much greater contaminating influence on the iron in the blast furnace or cupola.

After the foregoing determinations have been made, the ferrous sulfide, sulfate, and free-sulfur content of the coke will be known. By subtracting the sum of these, in terms of per cent of sulfur, from the total sulfur in the coke, the percentage of solid-solution sulfur will be known, and the analysis will be complete.

ACKNOWLEDGMENT

The writer wishes to extend his thanks to A. C. Fieldner, supervising fuels chemist of the Pittsburgh Experiment Station of the Bureau of Mines, under whose general supervision the present investigation was conducted.

Determination of Total Sulfur in Rubber Goods[1,2]

By S. Collier, Michael Levin, and R. T. Mease

BUREAU OF STANDARDS, WASHINGTON, D. C.

The Bureau of Standards method, by Waters and Tuttle, for the determination of sulfur in rubber goods has been modified as follows: Fifteen cubic centimeters of nitric acid-bromine mixture added to the sample and evaporated to dryness. Three cubic centimeters of nitric acid and 5 grams of sodium carbonate are added and the resulting mixture is dried and fused. The fused mass is lixiviated with water, filtered, the filtrate acidified with hydrochloric acid, and diluted to 300 cc. and the sulfur determined in the usual manner.

The amounts of occlusion, when the methods of the Bureau of Standards and of Kratz, Flower, and Coolidge are used, were determined by precipitating barium sulfate from solutions containing the equivalent amount of salts usually present, and varying amounts of pure sodium sulfate. The results show that the amount of occluded salts must be corrected for in accurate work.

The sulfur in several compounds, containing litharge and barytes, was determined by both methods. After correction for occlusion, the results obtained by either method are practically the same and sufficiently accurate.

THE method for the determination of total sulfur in rubber goods, which was devised by Waters and Tuttle,[3] has been used in the laboratory of the Bureau of Standards for a number of years.

In this method 0.5 gram of rubber is treated with 20 cc. of concentrated nitric acid saturated with bromine. After digesting for one hour in the cold and one hour on the steam bath, the excess of acid is evaporated off. To the residue are then added 5 grams of a mixture of equal parts of anhydrous sodium carbonate and potassium nitrate and enough water to make a pasty mass, which is spread on the sides of the crucible and dried on the steam bath. The crucible and contents are then heated over a sulfur-free flame until all carbonaceous matter is burned. The melt is cooled, lixiviated with water, the solution filtered, acidified with hydrochloric acid, and the sulfuric acid precipitated by the addition of barium chloride solution.

Recently, some work[4] was done to revise this method in order to save time without diminishing its accuracy. This work was based on the determination of sulfur in oils by Waters.[5] In the method as finally adopted 5 cc. of nitric acid-bromine mixture and 5 drops of bromine were used. After heating on the steam bath the excess acid was neutralized with sodium carbonate, thus avoiding the evaporation of the nitric acid and the use of a fusion mixture of potassium nitrate and sodium carbonate. Also the time for lixiviation was shortened and the final volume of the solution decreased. In addition, some work was done on the amount of occluded salts, because the work by Allen and Johnston,[6] Johnston and Adams,[7] and Waters[5] clearly showed that the amount of salts occluded by the barium sulfate precipitate should be taken into consideration, if accurate results are to be obtained.

Subsequently, in the use of this shortened method, it was found that some samples were so violently attacked by the nitric acid-bromine mixture that inaccurate results were obtained. The amount of acid left to be neutralized varied also, so that the resulting fusion mixture was not always of the same composition. It was decided that more work should be done to determine how little nitric acid-bromine mixture will suffice for all types of compounds.

Shortly after this work was started, the Committee on Methods of Analysis of the Rubber Division of the AMERICAN CHEMICAL SOCIETY[8] tentatively accepted as standard the methods of the Bureau of Standards and of Kratz, Flower, and Coolidge. It was decided to obtain some data on these methods and the amounts of occlusion, before finally adopting them, in order to eliminate doubt as to their value.

The work was divided into the following parts: the study of the effect of varying the amounts of nitric acid-bromine mixture; the determination of the degree of occlusion to be expected in the two methods; and the comparison of results obtained by both methods.

EFFECT OF DIFFERENT AMOUNTS OF NITRIC ACID-BROMINE MIXTURE

The following method was used in this work, except that the amount of nitric acid-bromine mixture was varied:

Place 0.5 gram of rubber in a porcelain crucible of about 75-cc. capacity, add 20 cc. of the nitric acid-bromine mixture, cover the crucible with a watch glass, and let it stand for one hour in the cold. Heat for an hour on the steam bath, remove the cover, rinse it with a little distilled water, and evaporate the solution to dryness. Add 3 cc. of nitric acid,

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[1] Received February 23, 1923.

[2] Published by permission of the Director, U. S. Bureau of Standards.

[3] *Bur. Standards, Tech. Paper* **174**; THIS JOURNAL, **3**, 734 (1911).

[4] Levin and Collier, *Rubber Age and Tire News*, **9** (2), 47 (1921).

[5] *Bur. Standards, Tech. Paper* **177**; THIS JOURNAL, **12**, 482, 612 (1920).

[6] *J. Am. Chem. Soc.*, **32**, 588 (1910).

[7] *J. Am. Chem. Soc.*, **33**, 829 (1911).

[8] THIS JOURNAL, **14**, 560 (1922).

cover, warm a short time on the steam bath, then let it cool. Carefully add in small portions, by means of a glass spatula, 5 grams of sodium carbonate (weighed to 0.5 gram). Raise the watch glass only high enough to permit the introduction of the spatula. Allow the carbonate to slide down the side of the crucible and not drop directly into the acid. Rinse the watch glass with 2 or 3 cc. of hot distilled water, and stir the mixture thoroughly with a glass rod. Digest for a few minutes, spread the mixture half way up the side of the crucible to facilitate drying, and dry on a steam bath. Fuse the mixture by heating over a sulfur-free gasoline flame, as follows: Place the crucible in an inclined position on a wire triangle and start the ignition over a low flame. The tendency for the rubber to burn too briskly is controlled by judicious use of the stirring rod with which the burning portion is scraped away from the rest. When part of the mass is burned white, work a fresh portion into it, and so on until all the organic matter is destroyed. It is necessary to hold the edge of the crucible with tongs. Toward the last half of the operation the flame should be increased somewhat, but it is never necessary to heat the crucible to redness. With care a crucible can be used for at least 10 or 12 fusions.

TABLE I—EFFECT OF VARYING AMOUNTS OF NITRIC ACID BROMINE MIXTURE ON PERCENTAGE OF SULFUR

No.	20 Cc.	10 Cc.	5 Cc.	5 Cc. + 2 Drops of Bromine	5 Cc. + 5 Drops of Bromine	5 Cc. + 8 Drops of Bromine
1	8.10 7.99	7.95 7.77	.. ..	7.81 7.42	.. ..	.. ..
	7.89 7.94	7.96 8.02	.. ..	7.77 7.47	.. ..	.. ..
	7.95 7.94	7.99 7.86	.. ..	7.51 7.66	.. ..	.. ..
	8.07 7.88	8.06 7.93	.. ..	7.91 7.42	.. ..	.. ..
	8.13 7.93	7.69 7.93	.. ..	7.33 7.86	.. ..	.. ..
	8.13 7.97	7.83 8.07	.. ..	7.14 ..	.. ..	.. ..
Av.	8.00	8.00		7.58		
2	6.03	5.68	5.68 5.67	5.70 5.66	5.72 5.74	5.72 5.66
	6.07	5.89	5.64 5.55	5.68 6.19	5.73 5.60	5.61 6.14
	6.10	5.88	5.66 5.62	5.70 6.12	5.56 5.59	5.71 6.04
			5.72 5.72	5.66 6.08	5.77 5.14	5.68 6.12
			5.48 ..	5.69 ..	5.89 ..	5.80 ..
Av.	6.07	5.82	5.64	5.85	5.63	5.85
3	7.75 7.85	7.88 7.64	.. ..	.. ..	.. ..	.. ..
	7.86 7.95	7.69 7.78	.. ..	.. ..	.. ..	.. ..
	7.77 7.93	7.86 7.90	.. ..	.. ..	.. ..	.. ..
	7.66 7.73	7.86 7.76	.. ..	.. ..	.. ..	.. ..
	7.88 7.80	7.64 7.66	.. ..	.. ..	.. ..	.. ..
	7.92 7.69	7.59 7.66	.. ..	.. ..	.. ..	.. ..
	7.81 7.69	7.66 7.58	.. ..	.. ..	.. ..	.. ..
	7.80 7.69	7.52 ..	.. ..	.. ..	.. ..	.. ..
Av.	7.80	7.71				
4	9.47 9.62	9.61 9.53	.. ..	.. ..	.. ..	.. ..
	9.58 9.60	9.64 9.37	.. ..	.. ..	.. ..	.. ..
	9.48 9.62	9.47 9.53	.. ..	.. ..	.. ..	.. ..
	9.56 9.45	9.56 9.61	.. ..	.. ..	.. ..	.. ..
	9.62 9.64	9.39 9.46	.. ..	.. ..	.. ..	.. ..
	9.60 9.55	9.37 9.35	.. ..	.. ..	.. ..	.. ..
	9.62 9.75	9.51 9.51	.. ..	.. ..	.. ..	.. ..
	9.45 9.67	9.41 9.38	.. ..	.. ..	.. ..	.. ..
Av.	9.60	9.49				

After the fusion, allow the crucible to cool, place it in a 400-cc. beaker, add sufficient distilled water to cover the crucible (about 125 cc.), and digest on the steam bath for 2 hours, with occasional stirring. If the filtration cannot be made in the same day, do not add the water, but allow the melt to stand over night to prevent the reversion to sulfate of any barium carbonate formed during the ignition.

Filter the solution into a covered 40-cc. beaker containing 5 cc. of concentrated hydrochloric acid, and wash the residue thoroughly with hot water. (A qualitative test for barium sulfate can be made on the residue.) Now, complete the acidification of the filtrate and washings and add 2 cc. of concentrated hydrochloric acid in excess. Cover the beaker and heat the solution on the steam bath. The total volume of the solution should not exceed 300 cc. The solution must be acid to Congo paper in order to insure the complete destruction of the carbonates. Precipitate by adding all at once 10 cc. of 10 per cent barium chloride solution, and determine the sulfur in the usual manner.

This method was varied by using 10 or 5 cc. of nitric acid-bromine mixture, or 5 cc. of nitric acid-bromine mixture with 2, 5, and 8 drops of bromine in place of the usual 20 cc. nitric acid-bromine mixture.

Table I shows that results obtained with 5 cc. of acid mixture and varying amounts of bromine are lower than those obtained by using 10 and 20 cc. of acid mixture. The table also shows that slightly lower results are usually obtained with 10 cc. of acid as compared with 20 cc., although the differences would fall within the usual range of experimental error.

More data were then obtained on two additional compounds by the use of 10, 15, and 20 cc. of nitric acid-bromine mixture. Compound A contained 4.3 per cent of free sulfur, and Compound B contained 8.5 per cent of antimony as sulfide and 3.8 per cent of free sulfur. The results given in Table II indicate that at least 15 cc. of nitric acid-bromine mixture were necessary. However, when compounds like those above are used, it is necessary to permit the oxidation process to go slowly.

TABLE II—FURTHER DATA ON EFFECT OF NITRIC ACID-BROMINE MIXTURES ON PERCENTAGE OF SULFUR

Compound	10 Cc.	15 Cc.	20 Cc.
A	9.48 9.36	9.81 9.68	9.91 9.75
	9.61 9.19	9.87 9.50	9.84 9.78
	9.59 9.44	9.86 9.71	9.87 9.75
	9.72 9.60	9.89 9.62	9.87 9.75
Av.	9.50	9.75	9.82
B	11.12 11.14	11.18 11.21	11.21 11.17
	11.15 10.92	11.15 11.10	11.32 11.14
	11.10 10.91	11.12 11.01	11.37 11.14
	11.06 10.92	11.09 11.21	11.40 11.18
Av.	11.04	11.14	11.25

DETERMINATION OF OCCLUSION

The degree of occlusion depends upon the nature and concentration of the salts in solution, on the acidity, and on the rate of the precipitation of the barium sulfate. As previously stated, the following work was based on that by Allen and Johnston and Johnston and Adams, who suggest, as a convenient way to obtain the correction for occlusion, the precipitation of barium sulfate from solutions containing known amounts of soluble salts and free acid, to which have been added definite weights of sodium sulfate dried at 200° C. for 2 hours. The differences between the weights of barium sulfate found and those calculated from the amount of sodium sulfate are the corrections.

The corrections for occlusion were determined by using varying amounts of a standard solution of sodium sulfate equivalent to the percentages of sulfur encountered in rubber analysis. The purity of the salt was determined by diluting and acidifying 5 cc. of the standard solution equivalent to 0.0821 gram of barium sulfate, and precipitating the barium sulfate in the usual manner. The amount of barium sulfate found was 0.2 mg. greater than the theoretical amount.

BUREAU OF STANDARDS METHOD—To a solution of 5 grams of sodium carbonate, 3 cc. of concentrated nitric acid were added, so as to have in the solution approximately the amount of nitrate left after an actual fusion. The remaining sodium carbonate was neutralized with concentrated hydrochloric acid and 2 cc. were added in excess. The barium sulfate was precipitated and determined in the usual manner.

The weights of barium sulfate were corrected for sulfate found by blank tests on the reagents, which usually amounted to 0.3 to 0.6 mg. of barium sulfate. The differences between the weights of barium sulfate found and the theoretical amounts represent the desired corrections for occlusion, which are given in Table III. If the found and theoretical weights of barium sulfate are plotted, an approximately straight line is obtained.

KRATZ, FLOWER, AND COOLIDGE METHOD—The method by Kratz, Flower, and Coolidge[9] given below was used, except that the rubber sample was left out and the desired amount of sodium sulfate solution was added to the filtrate just before the sulfur was precipitated.

Place a 0.5 gram sample in a 500-cc. Erlenmeyer destruction flask (Pyrex glass). Add 10 cc. of zinc nitrate-nitric acid solution prepared by dissolving 200 grams of zinc oxide in 1 liter of concentrated nitric acid, and whirl the flask rapidly to moisten the sample thoroughly. If convenient, this mixture may be allowed to stand over night. By so doing the sample becomes partly decomposed; this permits the addition of fuming nitric acid with no danger of ignition of the sample. Add 15 cc. of fuming nitric acid, and whirl the flask rapidly to keep the sample immersed and so avoid ignition by too rapid oxidation. With some samples it will be found necessary to cool the flask under a stream of tap water.

When the solution of the rubber is complete, add 5 cc. of a saturated water solution of bromine, and slowly evaporate the mixture to a foamy sirup. (For the determination of total sulfur in unvulcanized mixtures, use 3 cc. of bromine in place of bromine water.)

If particles of organic matter remain at the end of the evaporation, add a few cubic centimeters of fuming nitric acid and reëvaporate as before. Cool, and add a few crystals of potassium chlorate to assist in the oxidation of the sulfur and the decomposition of any nitrates.

Place the flask on asbestos gauze and evaporate the mixture to dryness over a Tirrill burner. Then bake the mixture at the highest temperature of the burner until all nitrates are decomposed and no more nitrogen peroxide fumes can be detected. (Care should be taken to insure uniform penetration of the heat throughout the contents of the flask and to remove the flask as soon as the baking is complete.) When the baking is complete, cool the flask, add 50 cc. of (1:6) hydrochloric acid, and heat until solution is complete. In case the original mixture contains barytes it will remain behind at this point. If there was any barium carbonate in the rubber compound it will be converted into the sulfate and the value for the total sulfur will be correspondingly low. If litharge is present in the mixture, lead salts, not otherwise removed, will be eliminated in the final washing with boiling water. Filter the solution, dilute to 300 cc., heat on the steam bath, add all at once 10 cc. of 10 per cent barium chloride solution, and complete the determination of the sulfur in the usual manner.

TABLE III—CORRECTIONS FOR OCCLUSION, IN PER CENT

Theoretical	Sulfur Found Min.	Max.	Av.	Average Occlusion Based on Sulfur Present	Average Occlusion Based on 0.5-Gram Sample
	Bureau of Standards Method				
2.25	2.26	2.40	2.32	3.1	0.07
9.02	9.18	9.43	9.27	2.7	.25
13.52	13.66	13.97	13.87	2.6	.35
17.66	...	...	17.96	1.5	.30
	Kratz, Flower, and Coolidge Method				
2.25	2.33	2.43	2.39	6.1	0.14
9.02	9.15	9.26	9.22	2.2	.20
13.52	13.68	13.78	13.75	1.7	.23

The weights of barium sulfate were corrected for sulfates found by blank tests on the reagents, which usually amounted to 2.5 to 4.5 mg. of barium sulfate. The differences between the weights of barium sulfate found and the theoretical amounts represent the desired corrections for occlusion, which are given in Table III. If the found and theoreticals weight of barium sulfate are plotted, an approximately straight line is obtained.

Each of the values in Table III represents the average of several determinations. The variation between the individual results usually checked within 0.2 mg. of barium sulfate.

From the results given in Table III, the following conclusions may be drawn:

The total sulfur, when determined by either method, should be corrected for the occluded salts.

The percentage of occlusion is greater for small amounts of sulfur when the Kratz, Flower, and Coolidge method is used. However, the results show that for all practical purposes there is not much difference in the amount of occlusion found by the two methods.

TABLE IV—COMPARISON OF TWO METHODS

	Per cent Sulfur: Bureau of Standards		Per cent Sulfur: Kratz, Flower, and Coolidge	
Theoretical	4.35	4.33	4.19	4.13
Found [a]	4.33	4.27	4.24	4.14

[a] Each value given in this table represents an average of four determinations in which the maximum deviation was 0.05 per cent.

TABLE V—RESULTS OBTAINED ON TWO VULCANIZED COMPOUNDS

No.	Approximate Compound Per cent		Per cent Sulfur, Corrected for Occlusion: Bureau of Standards				Kratz, Flower, and Coolidge			
1	Rubber	84.5	7.24	7.18	7.20	7.26	7.16	7.21	7.18	7.22
	Sulfur	7.0	7.22	7.18	7.16	7.18	7.10	7.10	7.18	7.00
	Litharge	8.5								
2[a]	Rubber	32.0								
	Barytes	61.0	2.54	2.38	2.54	2.52	2.50	2.56	2.59	2.44
	Sulfur	2.5	2.37	2.54	2.46	..	2.42	2.45	2.42	..
	Litharge	4.5								

[a] Percentage of sulfur, exclusive of sulfur as barytes.

COMPARISON OF RESULTS OBTAINED BY TWO METHODS

The sulfur of various compounds containing litharge and barytes was determined by the Bureau of Standards and the Kratz, Flower, and Coolidge methods, for it seemed that these compounds would be the most difficult ones encountered. The sulfur was first determined on an uncompounded mixture containing approximately 81 per cent of rubber, 15 per cent of litharge, and 4 per cent of sulfur. The sulfur was added in the form of sodium sulfate. Blank determinations were also made on the ingredients. The results, given in Table IV, show that the Bureau of Standards method tends to give slightly low values, and the Kratz, Flower, and Coolidge method slightly high values compared with the theoretical, although the errors are so small that both methods may be said to give accurate results. Confirmation of this statement is afforded by the results obtained on two vulcanized compounds (Table V).

Industrial Outlook Optimistic

The Industrial Employment Information Bulletin of the Department of Labor for August 20, 1923, shows a big upward swing in employment conditions for July, 1923, over July, 1922. The increases in percentage in thirteen of the basic industries on July 31, 1923, over July 31, 1922, are as follows:

Railroad repair shops	60.6
Beverages	49.7
Iron and steel and their products	25.7
Stone, clay, and glass products	25.5
Chemicals and allied products	18.6
Miscellaneous industries	18.02
Vehicles for land transportation	17.6
Textiles and their products	15.5
Metal and metal products other than iron and steel	10.2
Lumber and its manufacture	9.7
Leather and its finished products	8.1
Paper and printing	6.9
Food and kindred products	3.7

This analysis is based on information gathered each month by the special agents of the Department of Commerce in sixty-five industrial centers, and would seem to indicate that we are back to a sound and firm foundation that is wholesome and basically healthy.

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[8] *India Rubber World*, **6**, 356 (1920).

A Practical Solution of the Problem of Dewatering Activated Sludge[1]

By J. A. Wilson, W. R. Copeland, and H. M. Heisig

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The activated sludge process of sewage disposal was adopted by Milwaukee because the effluent is run directly into Lake Michigan, the source of its drinking water, and must, therefore, be purified to the highest degree attainable. The plant is designed to treat 85,000,000 gallons of sewage daily, from which 1,275,000 gallons of sludge, containing 98 per cent of water, are obtained. Although this process furnishes an effluent of the desired purity at all times of the year, it possessed one weak point at the time of its adoption—namely, the extreme difficulty of dewatering the waste sludge during the winter season. Chemical investigations carried out at the Milwaukee station over a period of several years have led to a successful solution of the problem of dewatering winter sludge. It was found that relatively enormous increases in efficiency of filter-pressing the sludge can be obtained by properly adjusting the temperature and pH value of the sludge and the amount of solid matter delivered per unit of filter area, and by adding aluminium sulfate followed by a corresponding adjustment of pH value.

THE present investigation is part of a larger work undertaken for the purpose of increasing the efficiency of operation of the activated sludge process by bringing about a clearer understanding of its fundamental mechanism. Some phases of this work have been reported in earlier papers.[2,3] In this process the raw sewage, after being screened, is passed into aeration tanks containing activated sludge and sewage through which air is forced in streams of tiny bubbles. This is accomplished by having the bottoms of the tanks fitted with Filtros plates, through which the air is forced. As the particles of sludge are knocked about by the air, they occlude bacteria and suspended matter from the incoming sewage. The mixture travels the length of the aeration tanks and finally enters a thickener, where the clear water, freed from more than 95 per cent of the bacteria and suspended matter from the original sewage, is decanted from the sludge and allowed to flow into the lake. The concentrated sludge, augmented by the bacteria and suspended matter from the sewage, is drawn out from the bottom and divided, part being returned for mixing with the incoming raw sewage and the rest being sent to be dewatered so that it may be shipped away as fertilizer. The dewatering operation is divided into two parts—filter-pressing to reduce the water content of the sludge from about 98 per cent to less than 80 per cent, and then reducing the water content further, to about 10 per cent, by the application of heat in a drier.

The waste sludge obtained in the summer time parts with its water easily and has never presented any serious difficulty in filter-pressing. In the winter time the sludge obtained is of a very different character, clinging tenaciously to its water and resisting filter-pressing. The condition of the sludge for dewatering by means of filtration passes through a yearly cycle; in February it is most difficult to filter, but as the weather gets warmer it filters more and more easily until September, when it is at its best. From September to February the sludge filters with increasing difficulty. Under fixed conditions, it takes about twenty times as long to filter a given quantity of sludge in February as it does in September. The sludge produced in cold weather quickly becomes septic and its solid contents dispersed to such a degree as to clog and blind the filter cloths.

RELATIVE FILTERING EFFICIENCY

The laboratory equipment used to study the effect of change of each of the several variable factors upon the condition of sludge for filtering consists of a battery of Büchner funnels set in filter flasks, all connected to one pump furnishing a high vacuum. When the sludge in the plant was in such condition that dewatering by means of a vacuum filter, under fixed conditions, was only just satisfactory, 500 cc. of the sludge diluted to contain 1 per cent of solid matter would filter through a standard laboratory filter in just 20 minutes. This made it convenient to define the *relative filtering efficiency* of a given sample of sludge as 2000 divided by the number of minutes required to filter 500 cc. of 1 per cent sludge through a standard laboratory filter. Changing the size of the Büchner funnels or the kind of filter paper employed merely changes the constant in the equation of proportionality between the small tests and the large-scale plant operation. Two years of operation of large-scale filter-pressings show that the efficiency obtained for any given type of sludge is directly proportional to the value defined as the relative filtering efficiency, provided the press is operated under fixed conditions, including the delivery of the same amount of sludge per unit of filter area in each pressing. The vacuum filter, designed for continuous operation, was found to be superior to all other types of filter presses tried, because it permits the regulation of the quantity of sludge applied to each unit of filter area to correspond to the condition of the sludge, which varies widely.

ANNUAL CYCLE

The lowest curve in Fig. 1 indicates the seasonal changes in the relative efficiency of filter-pressing the untreated waste sludge from the Milwaukee plant during the year. The curves do not show the rather wide daily fluctuations, but were plotted from series of averages obtained from daily tests over a period of more than two years. Only during a very short period, late in August and early in September, can the untreated sludge be filter-pressed in a reasonably satisfactory manner. The other curves show the seasonal changes in the sludge treated in ways before filtering that will be discussed presently.

An examination of sludge from the plant showed that the average size of the individual particles increases from February to September and then decreases. The fact that the average temperature of the sewage is lowest in February and highest early in September naturally led us to suspect that the condition of the sludge was determined by the temperature in the aeration tanks. Since other causes had been suggested as well for the improvement of the sludge in September, it appeared advisable to settle this point definitely. At the suggestion of T. Chalkley Hatton,[4] the experimental plant was divided into two independent systems at the beginning of the year 1922. One of these systems was operated in the normal manner and the other was operated exactly like it except for the fact that all the raw sewage entering it was heated to a temperature of 70° F. The sludge from the cold system, in which the temperature varied from 43° to 55° F., was characteristic of winter sludge. In the other system, however, the quality of the sludge at first became worse, but after about two weeks it began to improve and the average size of the particles began to increase until early in March the sludge was typical of the best ever obtained in September. The curves in Fig. 2 represent the relative filtering efficiency obtained when the pH value of the sludge was adjusted to 3.4 with sulfuric acid before filtering.

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[1] Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] THIS JOURNAL, 13, 406 (1921); 14, 128 (1922).

[3] *J. Am. Water Works Assoc.*, 8, 486 (1921).

[4] Chief Engineer, Milwaukee Sewerage Commission.

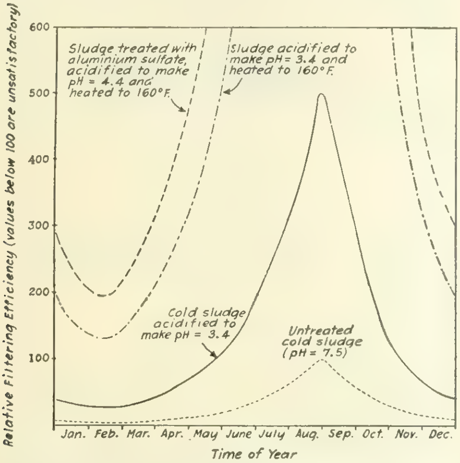

Fig. 1

Seasonal changes in the relative efficiency of filter-pressing activated sludge from Milwaukee sewage after treating in various ways. Sulfuric acid was used for acidifying the sludge and the pH values noted are those of the filter effluent. Sludge was heated only after acidifying.

The experiment shows clearly that the higher temperature assists in the building of large particles of sludge from the smaller ones. The decrease in quality of sludge during the first two weeks of January may be attributed to increased putrefaction in the thickener caused by the higher temperature. As the condition of the sludge entering the thickener improved, the tendency towards septic action decreased correspondingly.

Effect of pH Value

It is well known in the field of colloid chemistry that the tendency for particles of a dispersion to coalesce, forming larger ones, is markedly affected by change of pH value, the greatest tendency towards coalescence occurring at the isoelectric point. This is also the point at which organized jellies swell the least and most readily part with their water of imbibition. Although each amphoteric constituent of the sludge should be looked upon as having an isoelectric point of its own, not necessarily the same as that of the others, it is convenient to assume an isoelectric point of the sludge as a whole, which may be taken as that pH value at which the positive charges on the sludge just balance the negative ones. That this point will vary with the composition of the sludge is obvious.

The continuous curve in Fig. 3 shows the effect of decreasing the pH value of February sludge with sulfuric acid. Lowering the pH value to 3.4 causes an increase in relative filtering efficiency from 5 to 25. Although this is a large increase, it is the greatest possible with change of pH value alone, and is insufficient to bring February sludge into condition suitable for filter-pressing on a practical scale.

Considering the heterogeneous nature of the sludge, it is remarkable that the optimum filtering efficiency is obtained at pH = 3.4 the year round. The continuous curve in Fig. 1 shows the seasonal changes in rate of filtration of standard samples of sludge whose pH values have been adjusted to 3.4. Lowering the pH value from about 7.5 to 3.4, by adding sulfuric acid, multiplies the relative filtering efficiency by an average of about 5, regardless of the initial condition of the sludge—a fact of great practical importance since it enables us to filter-press the sludge satisfactorily from May to November simply by adjusting the pH value.

As would be expected, change of pH value also has an important effect upon the action in the aeration tanks. Ordinarily, the pH value of the liquor in the aeration tanks is about the same as that of the blood of living animals—7.4. It is possible that there is some relation between the building up and breaking down of tissues in the animal body and the actions proceeding in the aeration tanks. In a recent lecture on "The Chemical Mechanism of Atrophy in the Animal Body,"[5] H. C. Bradley pointed out that the stability of the body tissues is decreased when the oxygen supply is cut off and the pH value is allowed to fall by the introduction of acid. Immediately after the death of an animal there is a fall in the pH value of the blood from 7.4 to values below 7.0, and the tissues begin to atrophy. This action can be accelerated by the addition of acid, although an excess of strong acid retards the action.

When the air supply is cut off from the aeration tanks, the large particles of sludge immediately begin to break down. As in the case of animal tissues, adding just enough acid to bring the pH value to 6.0 caused the sludge particles to atrophy with extreme rapidity. The action is retarded by adding an excess of strong acid. However, if the pH value

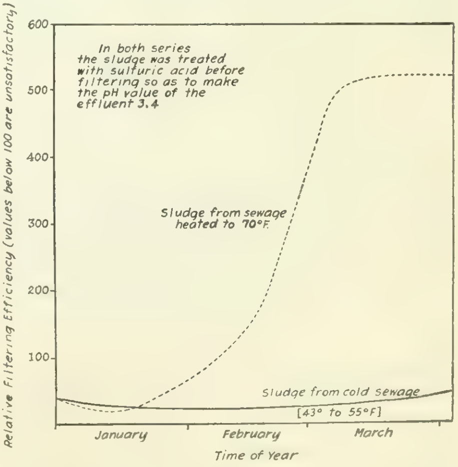

Fig. 2

Effect of heating raw sewage during the winter months upon the relative efficiency of filter-pressing the activated sludge produced. The aeration tanks were divided into two independent systems at the beginning of the year and all raw sewage entering one of them was heated to 70° F.

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[5] Delivered before the Milwaukee Section of the American Chemical Society, March 23, 1923.

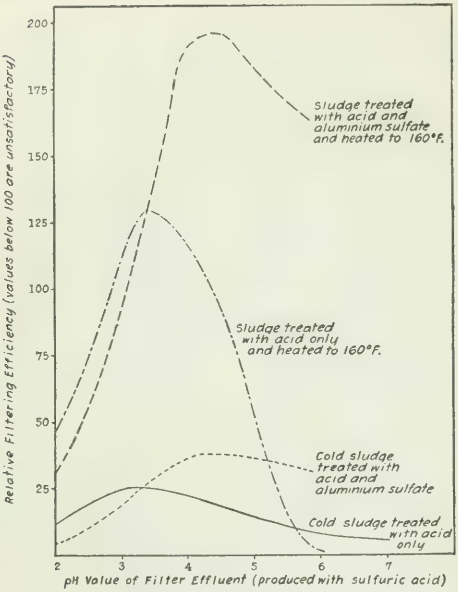

Fig. 3

Effect of change of pH value, produced with sulfuric acid, upon the relative efficiency of filter-pressing February sludge treated in various ways.

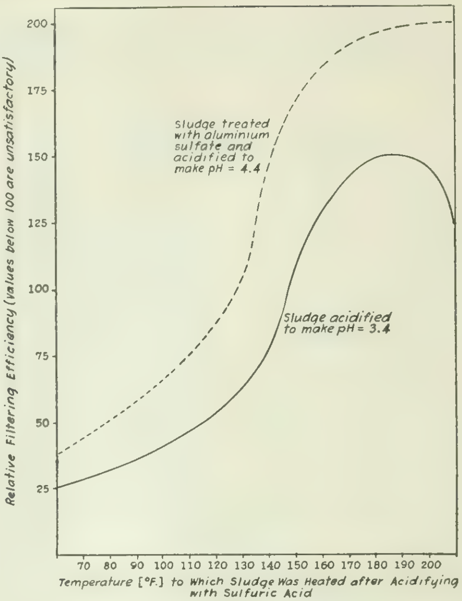

Fig. 4

Effect of rise of temperature upon the relative efficiency of filter-pressing February sludge at optimum pH value, with and without the addition of aluminium sulfate.

is again brought to 7.4 and the liquor aerated, the particles coalesce, reforming the large particles of the original liquor.

In aerating sludge at different pH values, two points were found at which large particles were built from the smaller ones, 3.4 and about 7.4. As the pH value increased from 3.4, this action became less pronounced and then reversed. Between pH = 5 and pH = 6 the particles rapidly disintegrated in spite of the aeration. Between the pH values 7 and 8 the air was again very effective in building up large particles. Below 3 and above 8 the air was without effect. It was also noticed that the putrefaction of protein matter in contact with an aqueous solution tended to cause the pH value of that solution to shift towards the region 5 to 6, regardless of the initial value.

At a pH value of 7.4, bubbling oxygen through the sludge causes a building of larger particles, while pure hydrogen causes a breaking down. At pH = 3.4, oxygen and hydrogen both show some tendency to cause a building of large particles, although oxygen is the more effective. When the initial sludge is already very septic, hydrogen may fail to show this building effect at pH = 3.4. Between 5 and 6 the disintegration of the particles proceeds rapidly regardless of the presence of oxygen or hydrogen.[6]

Apparently, a continual struggle is going on within the sludge, certain bacteria or enzymes present, which act best between the pH values 5 and 6, tending to break down the sludge. Outside of this range their action appears to be retarded by oxygen. At pH = 3.4, the apparent average isoelectric point of the sludge, the building up of the sludge particles is probably brought about by the forces of cohesion. Whether these forces alone are responsible for the action at 7.4 in the presence of oxygen may be questioned.

As the sludge particles disintegrate, they become more susceptible to putrefaction, probably because of the greater surface exposed to the action of bacteria and enzymes. The filter-pressing efficiency is also decreased because the smaller particles tend to clog the interstices of the filter cloth.

Effect of Temperature

While operating the vacuum filter in the plant, G. S. Backus tried heating sludge to a temperature of 160° F. after it had been acidified to make the pH value 3.4. A large and immediate increase in relative filtering efficiency was thereby obtained. But when untreated sludge was heated, its relative filtering efficiency rapidly decreased. The effect obtained is evidently a function of both temperature and pH value. One of the curves in Fig. 3 shows the effect of pH value upon sludge heated to a temperature of 160° F. The greatest beneficial effect is found at pH = 3.4. The heat is without effect at pH = 5.6, but above this value the heat is decidedly harmful. In each case the sludge was acidified before the application of heat. When the sludge is heated at its normal pH value of about 7.5, its condition becomes much worse. Bringing the pH value to 3.4 after heating improves its condition, but not nearly to the same extent as though it had been acidified before heating.

The seasonal changes in sludge acidified to make pH = 3.4 and then heated to 160° F. are indicated by one of the curves in Fig. 1. The combined effects of acid and heat cause the relative filtering efficiency to be multiplied by about 25 at all times of the year, thus making it possible to filter-press even February sludge in a satisfactory manner. The cost of the acid and heat for the purpose is not at all unreasonable.

If the effect of the high temperature were due to the coagulation of albuminous material, we should expect to find a break in the temperature curve. The continuous curve in Fig. 4 shows that no such break occurs; there is an increase in relative filtering efficiency for every degree rise of temperature from 60° to 190° F.

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[6] Compare This Journal, 14, 128 (1922), Fig. 2.

EFFECT OF ALUMINIUM SULFATE

A still further increase in relative filtering efficiency can be obtained by adding 1 pound of aluminium sulfate to every 50 gallons of waste sludge and adjusting the pH value to 4.4. The reason for the shift in optimum pH value to 4.4 may be explained by the necessity for the sludge to carry a negative electrical charge in order to co-precipitate the positively charged alumina. Fig. 3 shows that the optimum efficiency is obtained at 4.4, both for cold and heated sludge containing the aluminium sulfate. The effect of temperature upon the treated sludge at its optimum pH value is shown in Fig. 4, the best result being obtained at the boiling point of water.

The seasonal changes in sludge treated with aluminium sulfate, acidified to make pH = 4.4 and heated to 160° F., are shown in the top curve in Fig. 1. This treatment raises the increase in relative filtering efficiency to a grand total of about 4000 per cent.

The problem of dewatering activated sludge at all times of the year may, therefore, be considered as solved for the climate of Milwaukee.

Effect of Deaëration of Natural Waters on the Carbonate Equilibrium[1]

By D. H. Jackson and J. R. McDermet

ELLIOTT CO., JEANNETTE, PA.

In this paper it is shown that deaëration removes all free carbon dioxide and decomposes about 35 per cent of the bicarbonate present, most of it being precipitated and a small amount remaining in solution as calcium carbonate. The percentage bicarbonate removed increases slightly with increase in concentration of bicarbonate. The pH values are changed by deaëration from slightly acid to a fairly high alkaline value, the change averaging pH 2.5.

IN VIEW of the rather large volume of literature on aggressive carbon dioxide and hydrogen-ion concentration of natural waters, it was considered an appropriate and interesting problem to study the effect of deaëration of such waters on these factors. Experiments in this field should be especially significant at this time owing to the growing commercial interest in the application of apparatus for removing dissolved gases from water in systems where it is desired to prevent corrosion. The principal reason for removing dissolved gases is to eliminate the dissolved oxygen, which is the chief cause of corrosion of iron and steel by water. However, the carbon dioxide content should by no means be neglected, and the experiments recorded in this article were run with the idea of determining the change in hydrogen-ion concentration and the extent of bicarbonate removal when the free carbon dioxide in natural water is removed by complete deaëration.

DEAËRATION PROCESS

A complete description of this apparatus from both theoretical and practical standpoints is given by McDermet.[2] The deaërator to which the writers had access for running these tests is of the same type as is being extensively installed at the present time to prevent corrosion in power plants and hot-water service systems.

Before entering the deaërator, water must be heated to a minimum temperature of 160° F. The apparatus may be designed to handle water at any temperature from 140° F. up to the boiling point. Water enters the deaërator through a spring-loaded valve and passes through spray heads into a vacuum chamber. The spring-loaded valves tend to keep a constant pressure on the spray heads with change in water rate. The hot water entering the vacuum chamber is subjected to a process of explosive boiling at the expense of the heat it contains. The vacuum is regulated so that enough water is boiled to reduce the temperature of the water about 22° F., as this gradient has been found to produce perfect deaëration. The steam produced in the boiling process is drawn off into a small surface condenser which is cooled by the water going to the heater. The condenser is located so that the condensate drains back into the vacuum chamber and falls with the water from the spray heads over a series of cascade pans into the storage space in the bottom of the chamber. The water level in the chamber is regulated by a float-controlled valve. The vacuum is produced by an ejector of the steam jet type or by a motor-driven air pump connected with the condenser. In the former case an auxiliary condenser is used to recover the heat from the steam and the air extracted from the vacuum chamber passes through a vent to the atmosphere.

Water treated as above in practically all cases is delivered with an oxygen content of from zero to a trace, a trace meaning less than 0.02 cc. per liter as measured by the Winkler iodimetric method.

CARBON DIOXIDE TESTS

The water on which the carbon dioxide tests were run was the regular water supply of a power plant which takes water from a small stream about one mile north of Jeannette, Pa., and is characteristic of the water of the surrounding section. The water is used in the power plant without being filtered or otherwise treated than by the deaërator. Tests were run at different seasons of the year, so that the conditions could be varied as much as possible. A complete mineral analysis of this water might be of interest in connection with the experimental results of this paper, and a representative analysis is given in Table I.

TABLE I—ANALYSIS OF WATER TESTED

	PARTS PER MILLION		PARTS PER MILLION
Calcium	29.6	Chlorides	4.97
Magnesium	5.16	Carbonates as CO_2	71.4
Iron oxide	4.62	Sulfates	31.66
Alumina	3.10	Silica	9.81
Sodium	2.34	Organic matter	28.00
Ammonia	Trace	Suspended matter	16.7
Nitrites	Trace	Total solids	186.20
Nitrates	1.18		

pH = 6.8 maximum, 5.8 minimum

In connection with the test of deaëration on carbon dioxide removal, determinations of free carbon dioxide, bicarbonate, and carbonate were all carried out by titration, using the methods and precautions suggested by Johnston.[3] The

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[1] Received April 12, 1923.

[2] *Mech. Eng.*, **42**, 273 (1920).

[3] *J. Am. Chem. Soc.*, **38**, 947 (1916).

free carbon dioxide was titrated with 0.02 *N* standard sodium carbonate. This solution was carefully bottled and stored in such a way as to prevent it from coming in contact with the atmosphere. The bicarbonates and carbonates were determined by titrating with 0.02 *N* sulfuric acid, according to the methods and precautions mentioned above. As a check on the results, the total carbon dioxide was determined on many of the samples by measuring the volume of gas liberated by sulfuric acid in a Van Slyke apparatus and also by displacing all the carbon dioxide with acid, boiling, and determining gravimetrically by absorption in a Flemming bulb.

pH Determinations

The pH determinations were made with the aid of a hydrogen electrode against a mercury calomel cell and other standard equipment, which was periodically standardized against buffer solutions. Samples from the deaërator for pH determinations were placed in a beaker covered with a rubber diaphragm with three holes through it to accommodate the hydrogen electrode, the salt bridge of the calomel cell, and a motor-driven stirring device. Before the sample was introduced into the covered beaker, the latter was filled with hydrogen by displacement of water. The sample was then forced into the covered beaker by hydrogen pressure, entering through the hydrogen electrode without having had any chance to be polluted by the atmosphere. It might be suspected that the atmosphere of hydrogen over the sample while it is being stirred would have an appreciable effect upon the concentration of the other dissolved gases. This would doubtless be true if there were dissolved gases present, but both chemical and physical methods have been used in making determinations, and results are usually zero, or if any is found, the quantity is so small as to be negligible. In measuring the pH value of the raw water, samples were placed in an open beaker and run until the potentiometer reading was constant. Such results are probably slightly higher than they should be, owing to displacement of some of the carbon dioxide in solution by hydrogen from the electrode. However, the sample was in direct contact with the atmosphere while the determination was being made and equilibrium is supposed to exist between the two.

Determination of Total Calcium

The determination of total calcium was made on both raw and deaërated water to find out how much calcium was precipitated by deaëration. Results were obtained volumetrically by titrating the calcium oxalate with potassium permanganate and checked gravimetrically by weighing the oxide.

Comparison of Raw and Deaërated Water

Throughout the experiments for the comparison of raw and deaërated water, samples of raw water and of deaërated water were taken at practically the same time, the former being taken from the cold-water line to the heater and the latter from the deaërator discharge. In collecting samples from the deaërator, care was taken that there was no chance for pollution by contact with the atmosphere.

Results of Tests

All samples of water tested are on the acid side of neutrality, as shown by pH value from 6.85 downward. After deaëration the pH value ranges from approximately 8.8 to 9.5 and a good color change is always produced when phenolphthalein is added. This change is due to removal of carbon dioxide and partial decomposition of bicarbonate. When a sample containing phenolphthalein is stirred with a motor stirrer, it takes from 15 minutes to more than half an hour for the color to entirely disappear. It is observed to fade gradually away throughout the whole time. When the solution is allowed to stand in an open beaker, it takes from 6 to 48 hours for the color to fade away. It is evident, therefore, that it takes considerable time for the atmosphere to put back into the water the amount of carbon dioxide taken out by the deaërator in a fraction of a minute.

The results in Table II are representative of a large number of tests run as outlined in preceding paragraphs. The complete tests on samples showing the maximum amounts of bicarbonate are included in the table in order to emphasize the facts, as shown by the results, that the percentage removed increases with increasing concentration of bicarbonates.

In Table II no results are given for free carbon dioxide in deaërated water, for, as would be expected, free carbon dioxide cannot exist in water with the high pH values which all tests consistently showed on deaërated water. The higher pH values of deaërated water samples are partly due to the removal of all free carbon dioxide and partly to the formation of carbonate from a portion of the bicarbonate. The results show from 4.6 to 6.8 parts per million of carbon dioxide as carbonate in deaërated water. The solubility of calcium carbonate at 16° being 13 parts per million, which corresponds to 5.72 parts of carbon dioxide per million, it is evident that the solution has become saturated with carbonate and the excess, as indicated by the difference between the bicarbonate content of the raw water and the total carbon dioxide content of the deaërated water, has been precipitated. The difference on either side of the carbonate solubility point and the experimental results can be explained by changes in temperature or by adjustment of equilibrium after the water is deaërated and by the fact that small amounts of precipitated calcium carbonate may remain suspended in the solution. Suspended calcium carbonate was detected in samples of deaërated water by filtering and analyzing the residue.

The last sample in Table II was obtained from a different plant than the others and is well water. The pH values were determined with colorimetric indicator standards at the source of collection of the samples, and the titrations were run after the samples had been shipped to the laboratory. These analyses gave practically the same results as some of

Table II—Results of Tests for Carbon Dioxide, pH, and Total Calcium

Free Raw Water P. p. M.	Bicarbonate Raw P. p. M.	Bicarbonate Deaërated P. p. M.	Carbonate Deaërated P. p. M.	Total CO_2 Raw Water P. p. M.	Total CO_2 Deaërated Water P. p. M.	pH Raw Water	pH Deaërated Water	Calcium Deaërated P. p. M.	Calcium Raw P. p. M.
14.52	75.5	48.3	6.4	88.2	54.8	6.70	9.33	26.4	30.6
14.20	85.6	53.5	6.5	97.6	61.4	6.75	9.28	27.9	32.4
12.60	68.5	45.2	6.8	80.4	53.1	6.70	9.37	25.6	29.0
13.80	81.8	52.4	4.6	95.2	56.5	6.70	9.16	26.0	31.7
12.80	74.0	48.4	4.7	88.3	53.9	6.68	9.19	25.9	29.3
13.22	79.2	50.8	6.4	92.0	58.4	6.70	9.36	26.0	31.6
11.32	62.5	42.5	6.3	74.6	49.3	6.67	9.37	25.0	28.3
13.40	83.2	53.4	6.6	96.2	60.2	6.76	9.27	27.8	32.3
14.11	88.4	55.5	6.5	103.1	61.9	6.75	9.30	28.0	32.6
15.61	92.1	56.9	5.3	105.9	63.6	6.75	9.32	28.4	33.2
13.42	96.3	58.5	6.1	108.8	66.7	6.82	9.39	28.9	34.1
Average	78.2	54.6	6.0	....	....	6.70	8.70	27.1	30.5

the others, showing just a little less bicarbonate removed than any of the others, which was probably due to changes in the water after the samples were collected.

As a theoretical check on the analytical results of bicarbonate determinations in deaērated water, the following formula, as given by Massink and Heyman,[4] was used to calculate the bicarbonate content:

$$H^+ = 6 \times 10^{-11} \times \frac{\text{Bicarbonate } CO_2}{\text{Carbonate } CO_2}$$

H^+ being the hydrogen-ion concentration and the CO_2 values being expressed in milligrams per liter.

A comparison of the calculated results with the experimental results on the different samples in Table II are given in Table III.

TABLE III BICARBONATE CO_2—MG. PER LITER

EXPERIMENTAL	CALCULATED	EXPERIMENTAL	CALCULATED
48.3	50.1	42.5	45 2
53.5	57.6	53.4	59 2
45.2	48.1	55.5	53.6
52.4	49.3	56 9	60.1
48.4	50 4	58.5	62.1
50.8	47.0		

The results check fairly well, considering how much the value of the formula depends upon the accuracy of the pH measurements.

The results on calcium in raw and deaērated water show that an appreciable amount is removed by deaēration—not as much, however, as would be expected from the amount of bicarbonate removed. Indeed, there is not as much calcium present in either case as would be equivalent to the amount of bicarbonate found, showing that part of the bicarbonate is combined with other elements, probably magnesium.

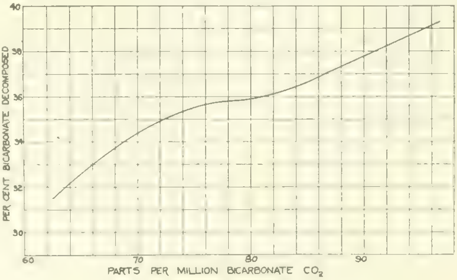

FIG. 1

To give an idea of the relative amounts of bicarbonate removed, a curve is given showing the total bicarbonate present in the raw water, plotted against the per cent removal by deaēration. The per cent removal is found to increase slightly with increase in concentration. It would be interesting to test the effect of deaēration on water with higher bicarbonate content, but it could not be done by the writer, as the laboratory was only convenient to the one power plant where deaērated water was available.

[4] *J. Am. Water Works Assoc.*, **8**, 239 (1921).

Substitution and Addition of Chlorine to the Rubber Molecule[1]

By J. McGavack

UNITED STATES RUBBER CO., NEW YORK, N. Y.

The main points in this brief paper are that substitution occurs first in an uncontrolled temperature reaction of chlorine with rubber; that, practically, substitution is complete before any addition occurs; that the procedure gives a quick method by which the rate of the chlorination of rubber may be determined at any particular time.

THE nature of the reaction of chlorine with hydrocarbons depends upon the temperature, light, and mechanical conditions, as well as upon the nature of the hydrocarbon itself. Saturated hydrocarbons can only react with chlorine by substitution. On the other hand, both substitution or addition may occur in the case of unsaturated hydrocarbons. For instance, the chlorination of toluene may result in entirely different chemical individuals, depending upon whether the reaction occurs in sunlight, diffused light, or at an elevated temperature. In the same manner the chlorinated products of ethylene may vary over a wide range, depending primarily upon the conditions under which the reaction is carried out. In fact, examples of this type are so frequent and familiar that it is useless to cite further cases.

For this reason it was thought that a dynamic study of the chlorination of the rubber hydrocarbon should be interesting and perhaps indicate the preference for substitution or addition. Previous workers, such as Gladstone and Hibbert,[2] have considered the chlorinated product of the rubber hydrocarbon from the end point only, and apparently have not dissected the reaction. The same is true of the work done by Peachy.[3] In general, all authorities practically agree, with the exception of Boswell, that the rubber hydrocarbon is an unsaturated aggregation of carbon and hydrogen. Boswell[4] claims that, instead of having a number of double bonds affording an opportunity for the addition of compounds like bromine and chlorine, we have internal linkages between the carbon atoms, thus causing complete saturation, and that the formation of double bonds of free valencies is only brought about when extreme or drastic treatment is employed. In any case, it was thought desirable to study this reaction from the dynamic standpoint.

The method (Fig. 1) consisted in passing a definite quantity of chlorine measured by a flowmeter (1) through a cylindrical vessel exposed to diffused light containing a known quantity of rubber cement. The effluent gases were cooled by means of a condenser allowing the solvent to return to the reaction chamber and were measured by means of a flowmeter (2). These gases were then washed thoroughly with water to remove any hydrochloric acid formed, measured by another flowmeter (3); and finally passed through strong alkali to absorb the final traces of chlorine. In this manner, by a simple glance at the flowmeter readings exactly what was occurring at any particular moment of the reaction could be determined. For instance, Flowmeter 1 measured the initial quantity of chlorine; Flowmeter 2, the chlorine unabsorbed plus hydrochloric acid given off by the reaction; and Flowmeter 3, the unabsorbed chlorine. By substracting the readings of 3 from those of 2 we would have the amount of hydrochloric acid given off at any particular time. Dividing this value by two, we would obtain the amount of chlorine substituted. The difference between the chlorine in and the chlorine out minus that substituted, of course, would give the value added.

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[1] Presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *J. Chem. Soc.* (*London*), **53**, 686 (1888).

[3] *J. Soc. Chem. Ind.*, **39**, 55 (1918).

[4] *India Rubber J.*, **64**, 981 (1922).

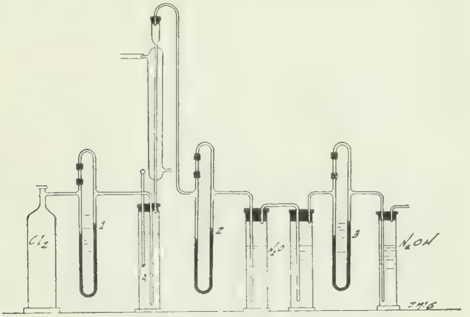

Fig. 1—Chlorination Apparatus

It is to be remembered that in such a process the results will vary as much as 3 per cent, inasmuch as flowmeters for measuring gases are probably only accurate to this degree. Furthermore, it should be stated that absorption of chlorine by the water-gas bottles was not taken into consideration, but it was thought sufficient to saturate first with chlorine the water thus used.

Experiment 17 gives a graphical representation of a typical experiment carried out in the manner described above. In this graph the gas volumes are plotted as ordinates against time as abscissas. Here we have a graphical record of the three different flowmeter readings, the area of which can either be integrated or calculated by inspection. Thus, that area between 1 and 2 gives the amount of chlorine absorbed; that between 2 and 3, the volume of hydrochloric acid given off, or twice the volume of chlorine substituted; while that between 3 and the abscissas gives the amount of chlorine lost. Unfortunately, the last area is inaccurate owing to the fluctuation of the temperature which allows for more or less absorption of chlorine by the solvent. On the other hand, that area representing the amount of hydrochloric acid given off is accurate to within the limits of the flowmeter readings.

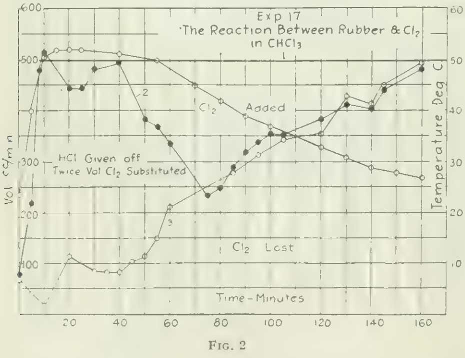

Fig. 2

It can easily be seen from this graph that substitution occurs during the first course of this reaction practically to the exclusion of addition. As the reaction proceeds the temperature decreases, substitution diminishes, and addition increases. This is also shown in Table I, which gives the results of nine experiments carried out in this manner.

Table I

Expt.	HCl Given Off Cc. at 25° C.	Pale Crepe G.	Solvent	Time of Run Min.	Rate of Chlorine Cc./Min.	Ratio HCl to Rubber in Mols	Chlorine Final Product %	Temp. Range ° C.
3	19,000	35	$CHCl_3$	140	580	2.98	65.1	51 to 25
4	18,740	35	$CHCl_3$	250	280	2.96	65.04	47 to 23
5	19,115	35	$CHCl_3$	280	280	2.99	65.45	48 to 23
6[a]	20,000	35	$CHCl_3$	385	280	3.11	64.55	30 to 6
15	19,500	35	$CHCl_3$	195	500	3.03	62.5	51 to 23
16	19,035	35	$CHCl_3$ Catalyst	100	500	2.97	...	54 to 30
17	20,700	35	$CHCl_3$	160	500	3.22	62.9	54 to 30
26	19,210	35	$CHCl_3$	155	500	2.99	...	52 to 23
12	12,700	35	CCl_4	265	500	1.98	60.0	61 to 20

[a] Reaction chamber surrounded by an ice bath.

It can be seen from a glance at Column 7, that the ratio of hydrochloric acid given off to the original amount of rubber when expressed in mols is approximately 3. This holds for all experiments, except Experiment 12, where this ratio is considerably less. This discrepancy is explained from the fact that with this experiment carbon tetrachloride in place of chloroform was used as a solvent. It is known that the solubility of the hydrochloride of rubber is approximately zero in this solvent, and hence what probably occurs in this case is, first, the addition of hydrochloric acid gas to the rubber molecule, precipitating a film of the hydrochloride on the rubber and thus preventing chlorination unless some mechanical stirring device is used. This reaction requires more detail than can be given in this brief note. It will also be seen from Column 8 that the percentage of chlorine in the final product is 65. If the chlorinated product does contain three atoms of substituted chlorine and four atoms of added chlorine, then the percentage of chlorine should be 65.1, which is in fair agreement with the experimental data. It may be seen also that the temperature was uncontrolled and that where the greatest substitution occurred there was the highest temperature. This is in agreement with known facts in regard to substitution and addition of halogens in hydrocarbons.

International Conference on Standardization

A conference of the secretaries of national industrial standardizing bodies was held in Zurich and Baden, Switzerland, July 3 to 7. Thirteen countries were represented, including all the more important industrial nations of Europe and America, P. G. Agnew being the delegate from the United States.

A leading topic discussed by the conference was the interchange of information between the various national bodies during the development of the work in the different countries. At the first conference, held in London two years ago, arrangements were made for the systematic interchange of completed work, and, to some extent, of information on work in progress. While it was not possible to overcome all the difficulties existing by virtue of the important industrial considerations involved, very substantial progress was made. It is believed that the steps taken will lead immediately to a substantially increased amount of interchange of information during the earlier stages of standardization work, and that the way has been paved for a much more extensive interchange in the future.

Provision was made for continuing the work of the conference on the many administrative problems of common interest, through a loose-knit continuing organization. An example of such work planned by the conference is the translation of technical terms of special importance or difficulty in standardization work. There will gradually be built up such a vocabulary of technical terms, mainly in English, French, and German, but supplemented as far as may be feasible and necessary by the corresponding terms in other languages.

Calculation of Flash Points for Pure Organic Substances[1]

By Edward Mack, C. E. Boord, and H. N. Barham[2]

Ohio State University, Columbus, Ohio

Thorton has shown that in a mixture of air and a combustible gas or vapor, the minimum explosive mixture contains about twice as many oxygen atoms and the maximum mixture about one-half as many oxygen atoms as are required for complete combustion.

It has seemed worth while to use this rule to calculate flash points for a number of pure substances. This is done by calculating from vapor pressure data the temperatures to which the substances in question must be brought in order that their saturated vapors will furnish mixtures with air which are just explosive. Unfortunately, the vapor pressure data are very meager. Flash points calculated in this way agree well with the observed values.

The work accomplished by Burgess and Wheeler[3] and by Thorton[4] in attempting to determine the relationship between the limits of inflammability of gaseous substances and their physical and chemical properties has a direct bearing on the subject of flash points. In fact, by making use of the relationship discovered by Thorton, the writers have been able to calculate the flash points of pure liquid and solid organic compounds when their vapor pressures are known in the region of the flash-point temperature. Thorton determined the relationship at both the upper and lower limits of inflammability. It may be stated as follows:

> In mixtures of paraffin hydrocarbons with air, there is twice the volume of inflammable gas at the upper limit of inflammability as in the mixture required for complete combustion; or, there are one-half the number of atoms of oxygen as are required for perfect combustion. At the lower limit of inflammability ignition fails when there are twice as many oxygen atoms per molecule of substance as are needed for perfect combustion, and first becomes possible when there is one less than this.

If M equals the number of molecules of the inflammable substance and N equals the number of oxygen atoms for complete combustion, then the upper limit mixture is $2M + N$, and the lower limit $M + (2N - 1)$.

For example, let us consider methane, which burns to carbon dioxide and water according to the equation

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

Here, $M = 1$ and $N = 4$. In the upper-limit mixture, therefore, there are two molecules of methane to every four atoms, or two molecules, of oxygen. The per cent by volume of methane in such a mixture is given by the expression $\frac{2 \times 100 \text{ per cent}}{2 + (2 \times 4.85)}$, where 4.85 is the number of volumes of air which will hold one volume of oxygen. The result is 17 per cent methane, as compared with an observed value of 14.8. For ethane the calculated and observed per cents are 10.5 and 10.7; for propane, 7.6 and 7.35; for butane, 5.9 and 5.7; for pentane, 4.9 and 4.5.

In the lower-limit mixture, with which one is more directly concerned in the calculation of flash points, there are $2N-1$, or 7 atoms of oxygen for every molecule of methane. The per cent by volume of methane is given by the expression $\frac{2 \times 100 \text{ per cent}}{2 + (7 \times 4.85)}$, and equals 5.5 per cent, as compared with an observed value of 5.6. For ethane the calculated and observed per cents are 3.08 and 3.1; for propane, 2.12 and 2.17; for butane, 1.62 and 1.55; for pentane, 1.31 and 1.35. While the two formulas $2M + N$ and $M + (2N - 1)$ are purely empirical, they give good results for benzene, and with slight modification for acetylene, ethylene, propylene, butylene, etc., cyanogen, carbon disulfide, methyl alcohol and ethyl alcohol, and many other widely different compounds.

Having found the per cent by volume of the inflammable substance in air which just gives an explosive mixture, the partial pressure of the inflammable substance may be calculated. For example, in the case of pentane, mentioned in the last paragraph, the partial pressure would be 1.31 per cent of 760 mm., or 9.96 mm. To obtain the flash point of pentane, it is then only necessary to find the temperature to which the liquid pentane must be brought in order that its saturated vapor will have a pressure of 9.96 mm. This temperature may be read off directly from the vapor pressure curve of pentane. In the tables given below are listed a number of flash points calculated in this way.

Observed Flash Points

When seeking a comparison between the calculated and observed flash points, one is confronted with the considerable disagreement of values obtained by the various flash-point testers in common use. Such disagreement is not at all surprising. Aside from the varying degrees of purity of the sample to be tested, a large part of it is due in the different cases, to (1) the employment of different sources of ignition—it by no means follows that an inflammable liquid will flash at the same temperature for an electric spark, as it will for a match flame, or a wick flame; (2) to the unsaturated condition of the vapor where ignition occurs; in some flash-point testers the vapor may be almost saturated, in others it is far from saturation.

A simple apparatus was constructed to determine actual flash points, having in mind these two fundamental points. The apparatus is shown in Fig. 1. The substance to be tested is placed in the large glass test tube, T, and the platinum points, S, forming a spark gap, are adjusted so that they are very near to the surface of the liquid. Air which has been dried by passage through a calcium chloride tube is allowed to flow slowly over the surface of the liquid, and serves the

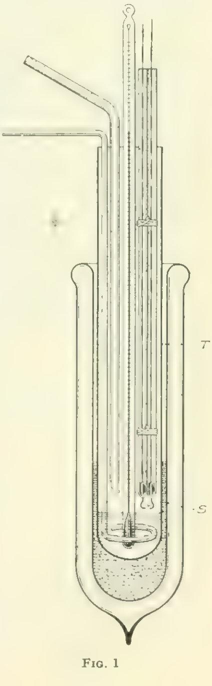

Fig. 1

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[1] Received March 19, 1923.

[2] The experimental part of this paper is abstracted from the thesis presented by H. N. Barham to the Graduate School of the Ohio State University in partial fulfilment of the requirements for the degree of Master of Science.

[3] *J. Chem. Soc.*, **99**, 2013 (1911).

[4] *Phil. Mag.*, **33**, 190 (1917).

double purpose of washing out the oxidation products of the preceding test, and of supplying oxygen. The rate of air flow is not great enough to disturb the liquid surface. The temperature of the substance is regulated so that the flash point can be approached from below, using either a Dewar flask with solid carbon dioxide and acetone for the outside bath, or a beaker of water heated with a Bunsen burner to the proper temperature, and testing at intervals of one degree or even fractions of a degree in the near neighborhood of the flash point itself. The temperature at which an almost invisible blue flame passes over the surface of the liquid is the flash point. It is best to view the flame against a dark background.

With every pure substance the flash point is sharp and distinct, and is reproducible within quite narrow limits (0.5 degree). Below the minimum explosive mixture the color of the spark is light blue, accompanied by no flash. The color of the spark above the maximum mixture is red (with no flash), the red color possibly being due to a luminescence of carbon set free by the partial combustion of the substance near the electrodes, in a small nonspreading zone of oxidation which exists there. Chemical reaction often takes place when the liquid is several degrees below the flash point, but such action is confined strictly to a small region about the spark gap, and the reaction does not propagate itself throughout the whole mixture. For instance, in the case of carbon disulfide, it is easy to see that chemical action is taking place in the spark gap at temperatures of −40° and −35° C., and the odor of sulfur dioxide is very strong; but no self-propagating flame is formed until the temperature has been raised to about −26° C.

The manner in which the flash point depends on the nature of the source of ignition is as yet not fully understood. In the case of the electric spark, which because of its reproducibility is probably the best means of ignition to employ in testing flash points, several investigators have suggested that it is the quantity of energy in the spark which is the determining factor in giving ignition.

Paterson and Campbell,[5] however, show that the potential of the spark discharge is much more important, and that if this is large the actual quantity of energy may be quite small and still give effective ignition. The ignition *may* depend on the material of which the electrodes are made, and *does* depend on the shape of the electrodes. Ignition occurs more readily when the spark discharge is between points.

In the apparatus described above the electrodes were of platinum and sharpened at the ends. An induction coil served as the source of current, with a battery of dry cells on the primary. A sufficient number of dry cells were used so that the addition of any more made no change in the flash point of the explosive mixture excited by the spark. With the induction coil used, three dry cells in series gave this condition.

COMPARISON OF OBSERVED AND CALCULATED FLASH POINTS

Table I shows the calculated and observed flash points for a number of common organic liquids and for a few solid substances.

Most of the vapor pressure data used in making these calculations have been taken from Landolt-Börnstein tables and the recent literature. In those cases where the vapor pressure data were not available, the vapor pressure has been calculated from the boiling point by the method of Lewis and Weber.[6] In making these calculations water has been used as the liquid of reference in the equation

$$\frac{\Delta T_w}{\Delta T} = \frac{L}{L_w}\left\{\frac{T_w}{T}\right\}^2$$

In the equation, T_w represents the boiling point (absolute) of water, and T the boiling point (absolute) of the substance whose vapor pressure is being calculated. L_w and L are the molal heats of vaporization of the water and the substance, respectively. ΔT_w is the difference in degrees between 100, the boiling point of water, and that temperature at which water has the same vapor pressure that the substance has at its flash point. ΔT is the difference in degrees between the boiling point of the substance and its flash point. The flash points calculated in this way have been marked with asterisks (*). Except in the one case of isopropyl alcohol, where the calculated flash point is 14 degrees lower than the observed value, the agreement between the calculated and observed points is remarkably good. These results seem to indicate that the flash point of any pure compound of the same general nature as those in the table can be calculated, *with nothing more known about the substance than its boiling point*, and, of course, its chemical formula.

TABLE I—CALCULATED AND OBSERVED FLASH POINTS

SUBSTANCE	M	N	Percentage Composition	Partial Pressure	Calcd. Flash Point	Observed Flash Point
Aliphatic hydrocarbons—Lower limit $M + (2N - 1)$						
C_6H_{14}	2	19	1.10	8.36	−27.5	−18.0
C_8H_{18}	2	25	0.84	6.38	12.0	17.0
Aromatic hydrocarbons—Lower limit $M + (2N - 1)$						
C_6H_6	2	15	1.40	10.64	−12.0	−9.0
$C_6H_5CH_3$	2	18	1.16	8.82	3.0	6.5
$C_6H_5C_2H_5$	2	21	1.00	7.60	21.5*	15.5
n-$C_6H_5C_3H_7$	2	24	0.87	6.61	35.5*	30.5
sec-$C_6H_5C_4H_9$	2	27	0.74	5.63	52 0*	52.0
$C_{10}H_8$	2	24	0.87	6.60	78.0	86.0
Aliphatic esters—Lower limit $M + (2N - 1)$						
$HCOOC_2H_5$	2	7	3.20	24.30	−19.0	−19.5
CH_3COOCH_3	2	7	3.20	24.30	−16.0	−15.5
$CH_3COOC_2H_5$	2	10	2.20	16.70	− 6.0	− 5.0
iso-$HCOOC_3H_7$	2	10	2.20	16.70	− 4.5*	− 5.5
n-$HCOOC_3H_7$	2	10	2.20	16.70	− 4.5	− 3.0
$C_2H_5COOCH_3$	2	10	2.20	16.70	− 3.5	− 2.0
iso-$CH_3COOC_3H_7$	2	13	1.70	12.92	4.0*	4.5
n-$CH_3COOC_3H_7$	2	13	1.70	12.92	9.0	14.5
$C_2H_5COOC_2H_5$	2	13	1.70	12.92	7.0	12.5
n-$C_3H_7COOCH_3$	2	13	1.70	12.92	9.0	14.0
n-$HCOOC_4H_9$	2	13	1.70	12.92	21.5*	17.5
Phenols—Lower limit $M + (2N - 1)$						
C_6H_5OH	2	14	1.50	10.6	76.0	79.0
o-$CH_3C_6H_4OH$	2	17	1.24	9.5	74.0	83.0
m-$CH_3C_6H_4OH$	2	17	1.24	9.5	84.0	86.0
p-$CH_3C_6H_4OH$	2	17	1.24	9.5	84.0	86.0
o-$C_6H_4(OH)_2$	2	13	1.62	12.0	130.0*	127.0
m-$C_6H_4(OH)_2$	2	13	1.62	12.0	158.5*	152.0
p-$C_6H_4(OH)_2$	2	13	1.62	12.0	165.0	165.0
Miscellaneous compounds—Lower limit $M + (2N + 1)$						
$C_6H_5NO_2$	2	14.5	1.45	11.02	89.0	88.0
C_6H_5COOH	2	15.0	1.40	10.64	133.5	131.0
Alcohols—Lower limit $M + (2N + 1)$						
CH_3OH	2	3.0	5.56	42.26	5.5	5.5
C_2H_5OH	2	6.0	2.51	19.10	7.0	9.0
n-C_3H_7OH	2	9.0	1.62	12.31	18.0	22.5
iso-C_3H_7OH	2	9.0	1.62	12.31	0.5*	14.5
n-C_4H_9OH	2	12.0	1.20	9.12	30.0	35.5
iso-C_4H_9OH	2	12.0	1.20	9.12	21.0	27.5
n-$C_5H_{11}OH$	2	15.0	0.95	7.22	33.0	...
iso $C_5H_{11}OH$	2	15.0	0.95	7.22	33.5	40.0
Carbon disulfide—Lower limit $M + (2N - 1)$						
CS_2	2	6.0	2.5	19.0	−28.0	−25.5

Generally, the calculated flash points are a little lower than the observed values. This may be attributed in certain instances to an unsaturated condition of the vapor, as, for example, is clearly the case for the solid substance naphthalene. In some other cases the vapor pressure data are of questionable reliability.

FLASH POINTS OF MIXTURES

The calculated and observed flash points recorded above have been for single compounds. The same method can be extended to a mixture, provided the components of the mixture are all in the same series. Consider a certain sample of gasoline which is a mixture of paraffin hydrocarbons, C_nH_{2n+2}. The formula $M + (2N - 1)$, which gives the composition of the minimum explosive mixture, holds for the first members of this series and also for the higher members. It must hold therefore for any mixture of these hydrocarbons. The number of oxygen atoms N required for perfect combustion may be found if the average molecular weight of the gasoline is known. Suppose, for example, that the average molecular weight is 107. By subtracting 2 (for the two hydrogen atoms at the end of the chain) and dividing the remainder by 14 (the sum of the atomic weights in the CH_2 group) the number of CH_2 groups in the average molecule may be obtained. Three times this number of oxygen atoms plus one for the two hydrogen atoms will be the number required for complete combustion. In the above case:

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[5] Collected Researches, The National Physical Laboratory, **15**, 237 (1920).

[6] THIS JOURNAL, **14**, 486 (1922).

$$3\left(\frac{107-2}{14}\right)+1=N=23.5$$

The percentage composition by volume of the minimum explosive mixture and the partial pressure are then calculated as before. The vapor presure of the mixture in the region of the flash point must be known. If an unknown percentage of the members of another series is also present in the mixture, there would be no way of finding the number of oxygen atoms required for complete combustion.

With mixtures it will generally be simpler to determine the flash points directly. But if the composition of the mixture is known and the vapor pressure data are available, the flash point may be calculated with an accuracy approaching that for the simple substances listed above.

Oxide Equilibria in Catalysis[1]

By **J. M. Weiss, C. R. Downs, and R. M. Burns**

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In view of the importance of vanadium oxide as a catalyst in the partial oxidation of benzene and naphthalene, a study was made of the composition of vanadium catalysts under various reaction conditions. The results help to throw light on the mechanism of these catalytic reactions and it is hoped that further studies along these lines will be made.

The use of vanadium oxide as an oxidation catalyst to cause the partial oxidation of aromatic hydrocarbons is a practical development of comparatively recent accomplishment. The most outstanding uses are the production of phthalic anhydride from naphthalene[2] and the production of maleic acid from benzene.[3] The mechanism of the action of the catalyst is of interest, and the present paper is a report of a few preliminary experiments which were an attempt to throw light on this question.

A catalyst may act in several different ways. In the case under consideration, one function of the catalyst appears to be that of furnishing activated oxygen. The actual process causing this activation may involve either the adsorption and subsequent evaporation of oxygen from the catalyst surface, or, more likely in this case, an oscillation from one oxide to another, yielding activated oxygen by the dissociation of the higher oxide. The process is debatable, but the actual composition of the oxides present at the end of reacting periods constitutes a fact capable of determination, and it seemed likely that such knowledge might be of value in understanding the mechanism of the catalysis.

The varying colors of the vanadium oxide catalyst—blue-green to orange—when removed from the reaction zone suggested that the degree of oxidation of the vanadium was decidedly affected by the reaction conditions. Five oxides of vanadium have been described: V_2O, brown; V_2O_2, gray; V_2O_3, black; V_2O_4, blue; and V_2O_5, reddish yellow. Under ordinary conditions the pentoxide is the stable form. Each oxide naturally has a definite dissociation pressure, which, of course, is exceedingly low for the normal temperatures.

Mixter[4] gives data for the heats of formation of the various oxides of vanadium, which, if reliable, serve to calculate the dissociation constants with a fair degree of accuracy, according to Nernst's approximation formula:[5]

$$\log P_{O_2} = -\frac{Q}{4.571\,T} + 1.75 \log T + C$$

where C = constant for oxygen = 2.8

T = absolute temperature

Q = heat of formation

On the basis of the heats of formation given by Mixter,[4] of 28,200 calories of V_2O_5 from V_2O_4 and 59,600 calories of V_2O_4 from V_2O_3, the following figures were obtained, expressed in atmospheres:

Temperature ° C.	$P_{O_2}(V_2O_5 \rightarrow V_2O_4)$	$P_{O_2}(V_2O_4 \rightarrow V_2O_3)$
0	10^{-15}	10^{-40}
400	0.038	10^{-11}
525	1.00	10^{-9}
1260	...	1.0

Vanadium pentoxide, V_2O_5, in equilibrium with the tetroxide, V_2O_4, and oxygen constitutes a univariant system. The trioxide, V_2O_3, may conceivably exist in equilibrium with this system at one temperature and pressure, the point where the pentoxide phase just disappears.

The addition of benzene vapor to the two oxide–oxygen system would be expected to disturb the equilibrium at those temperatures above which the rate of oxidation of benzene vapor becomes appreciable, since oxygen would be removed from the system. Under given conditions of temperature and benzene partial pressure, this oxygen removal may be fairly constant, causing as a result a definite increase in dissociation of the pentoxide. It would be predicted, therefore, that at a given temperature the percentage of vanadium tetroxide would be proportional to the partial pressure of benzene vapor for a given space-time velocity.

It would be unsafe to attempt to predict the form which the equilibrium would take under these conditions, so experiments were made.

EXPERIMENTAL

It was decided to hold the temperature constant at 400° C., which is a point corresponding to that for a favorable yield of maleic anhydride, and to determine the effect on the oxide equilibrium of varying the benzene-oxygen ratio.

The catalyst was held in the reaction tube placed in an agitated bath using lead as the bath material. The gases under investigation were measured by a wet drum meter and dried by means of concentrated sulfuric acid. The gases used were hydrogen, nitrogen, and air. In the benzene runs the air was loaded with a predetermined amount of benzene by passing it through a thermostatically controlled benzene vaporizer before it entered the catalyst tube. The gain or loss in weight of the catalyst was determined by weighing the reaction tube after allowing the preliminary heating to proceed at the desired temperature. When a constant weight had been reached it was known that the complex organic molecule, of which the vanadium was a part, had been decomposed. As the analysis of the mixed oxides was desired, no carrier for the catalyst was used.

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[1] Presented before the Division of Organic Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Gibbs and Conover, U. S. Patent 1,285,117 (November 19, 1919).

[3] Weiss and Downs, U. S. Patent 1,318,633 (October 14, 1919).

[4] *Am. J. Sci.*, [4] **34**, 145 (1912).

[5] Nernst, "Theoretical Chemistry," **1916**, p. 758.

A weighed sample was dissolved in dilute sulfuric acid and titrated with permanganate. The titrated solution, after reduction by means of SO_2 and boiling off the excess SO_2, was again titrated with permanganate. The difference between values of the two permanganate titrations gave the percentage of V_2O_4 present in the sample. Whenever V_2O_3 was present in the sample, the first titration with permanganate was greater than that after the SO_2 reduction, as SO_2 will not reduce V_2O_4 to V_2O_3.

RESULTS

The results are given in the following table:

No.	Ratio Weight Air to Weight Benzene	Duration of Test Hrs.	Absolute Pressure Atmos.	V_2O_5 %	Catalyst Composition before Test
1	14:1	5	1.00	94.3	60% V_2O_3, 40% V_2O_4
2	12:1	12	1.00	75.0	
3	11.3:1	6	2.06	82.6	
4	11.0:1	39	1.00	72.0	98.5% V_2O_5, 1.5% V_2O_4
5	10.6:1	23	1.00	80.0	
6	10.5:1	8	1.00	73.0	60% V_2O_3, 40% V_2O_4
7	10.5:1	10.5	1.99	82.7	98.5% V_2O_5, 1.5% V_2O_4
8	2.2:1	31	1.00	9.1	
9	2.6:1	22	1.00	11.8	60% V_2O_3, 40% V_2O_4

In addition, freshly prepared catalyst was heated to 400° C. in air at one atmosphere pressure (absolute). The final composition was V_2O_5, 98.5 per cent; V_2O_4, 1.5 per cent.

No runs were made with benzene vapor alone passing over the catalyst. In a current of hydrogen, however, at 400° C., the catalyst was reduced after 17 hours to the composition, V_2O_3, 86.0 per cent; V_2O_4, 14.0 per cent. The reduction of the vanadium oxide catalyst below V_2O_4 is thus very slow at this temperature in a hydrogen atmosphere, but if carried to completion with absolutely pure hydrogen, practically only V_2O_3 would result. It is of interest to note here that with hydrogen containing very small amounts of oxygen the rate of reduction has been found to be very materially decreased.

When the freshly prepared catalyst was heated to equilibrium at 400° C. in a closed tube, the composition was V_2O_3, 47.0 per cent; V_2O_4, 53.0 per cent. The explanation of this composition is that the catalyst was prepared as the vanadium salt of an organic acid, which under decomposition by heating produced a reducing atmosphere composed of carbon monoxide.

On the basis of the results obtained, an approximate curve showing the relation of catalyst composition to the ratio of oxygen to benzene has been drawn. As no results were obtained in the range between 3:1 and 11:1, the shape of the curve in this region is unknown, but it should lie somewhat to the right of a straight line connecting the determined points and take somewhat the shape of the curved line as shown. Above the limits of these results—that is, at greater ratios than 14:1—the curve must approach the vertical to correspond with the value for 0 per cent benzene, or pure air; consequently, the curve is extended vertically. The extension of the curve below the ratio of 2:1 must approach the horizontal, and at some, probably very low, oxygen concentration V_2O_5 will vanish and the equilibrium will exist between V_2O_4 and V_2O_3. At the transition point all three oxides will exist in equilibrium. Whether this triple point is close to the origin or not, is not known, but its accurate determination would be of great interest.

It will be seen by reference to the table that, although the composition of the catalysts used in Runs 2 and 6 contained no V_2O_5 initially, the analyses of the catalysts upon completion of the runs show their compositions to be practically the same as was found in Runs 4 and 5 where the catalysts employed contained 98.5 per cent of the pentoxide.

Runs 3 and 7 were made with the system at 2 atmospheres pressure, and, as would be expected, show somewhat higher percentages of the pentoxide owing to its decreased dissociation. Again, it is interesting to note that the catalyst used in Run 3, which was originally composed of 60 per cent V_2O_3 and 40 per cent V_2O_4, shows practically the same composition at the end of the run as that shown by the high pentoxide catalyst used in Run 7. The final equilibrium ratio of oxides is therefore approached from both directions.

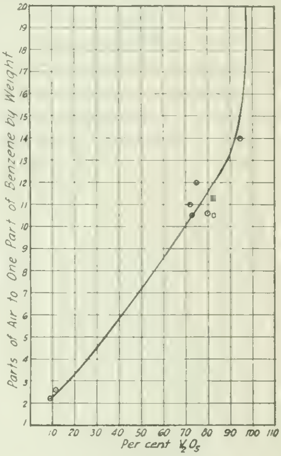

FIG. 1—RELATION OF CATALYST COMPOSITION TO OXYGEN-BENZENE RATIO

CONCLUSIONS

These results show that the composition of vanadium oxide at a given temperature and pressure depends upon the air-benzene ratio employed. Although the data given in this paper do not include information on the conversion of benzene to maleic acid, they assist in throwing some light on the mechanism of catalytic processes of this type, and some speculation here concerning this point seems to be in order.

Where the partial oxidation of organic compounds is under consideration, there are evidently other important factors besides the activation of oxygen. If the catalytic action depended entirely upon the activation of the oxygen, there would be no explanation of the action of different catalysts, some of which produce only products of complete combustion, while others produce mainly partially oxidized products, and still other compounds appear to be practically inert except at high temperatures, where their function can hardly be called truly catalytic. The writers would differentiate, therefore, between active catalysts, those producing mainly complete combustion at temperatures where any reaction at all results, and productive catalysts, those which produce partial oxidation products in substantial amounts, but at the same time appearing always to produce products of complete combustion.

The behavior of the catalyst strongly suggests that the mechanism of the catalysis involves an oscillation between V_2O_5 and V_2O_4—that is, the rate of reaction may be dependent upon the rate at which activated oxygen is supplied by the dissociation of the pentoxide.

At temperatures increasing above 400° C. with any given ratio of air to benzene, the proportion of V_2O_5 will progressively decrease, but the writers have found that complete combustion also increases at the expense of the partial oxidation products. The opposite is true of the lower temperatures. Therefore, the proportion of complete combustion is not dependent upon the ratio of V_2O_5 to V_2O_4, but upon some other factor such as the activation of the reacting substances. The reaction velocity of complete combustion apparently increases more rapidly than the reaction velocity of partial oxidation with increase in the temperature above a certain value. Again, if ratios greater than 14:1 are used, with the temperature fixed, say, at 400° C., the proportion of complete combustion products to partial oxidation products is not markedly increased. With these ratios the catalyst is almost entirely V_2O_5, and for this reason the ratio of V_2O_5 to V_2O_4 appears to have little effect upon the relative amounts of the different kinds of products.

The productivity of the catalyst, whether composed of oxides of a single metal or of several metals, seems to be a function of some undetermined property other than the mere activation of the oxygen by the dissociation of the oxide. It does not seem to depend on the crystal structure of the oxides as the degree of oxidation of the catalyst does not alter its specific effect. Apparently, however, there is a close relation between the crystal structures and dimensions of the metal atom and those of the organic compound and this specific catalytic action, the degree of oxidation of the catalyst at the end of the reaction being merely a result of the conditions obtaining in the system.

As the complexity and instability of the aromatic molecule increase, there appears to be a greater number of productive catalysts which yield partial oxidation products. The benzene molecule, being the most simple and stable, is partially oxidized only by oxides of vanadium, although mixtures of oxides, which alone do not give partial oxidation products of benzene, act in a similar manner. As yet there is no certain explanation of this peculiar action of mixed oxides. In the oxidation of naphthalene, anthracene, and the methyl benzenes a progressive increase in the number of catalysts which will produce partial oxidation products is noted.

It is hoped that this rather restricted resumé of catalytic oxidation of aromatic compounds will excite more extended interest, and that by a combination of the study of the atomic structure of catalysts and organic compounds, together with further studies of the specific action of catalysts, a clear path may be hewn through the confusing tangle now existent.

Solubility of Nickel Sulfate by Floating Equilibrium Method[1]

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The paper presents the application of the floating equilibrium method for the determination of the solubility of the various hydrates of nickel sulfate. The method consists in the determination of the quantity of water required to bring a solution saturated with the salt at a definite temperature to the same concentration as a gravimetrically standardized solution of nickel sulfate, the concentration of the latter determined by the condition of floating equilibrium of a glass float calibrated for the particular solution.

A description of the thermostats, thermoregulators, and solution apparatus is set forth. Data obtained show a close agreement with results obtained gravimetrically. The results are usually slightly higher by the floating equilibrium method than by the gravimetric methods.

The application of the principle of floating equilibrium to the determination of the solubility of the various hydrates of nickel sulfate is a modification of the principle as set forth by Richards and Shipley,[2] applied to precision thermometry. They used various concentrations of salts to affect equilibrium for noting accurate temperatures. Lamb and Lee[3] utilize somewhat the same principle in measuring the density of various solutions to an exceedingly high degree of accuracy, by measuring the weights and the amount of current sent through an electromagnet that will cause a 250-ml. inverted flask in which an iron rod is sealed to sink in the solution being studied. The application of floating equilibrium for the determination of the solubility of lead acetate was used by Dundon and Henderson.[4]

The application of the principle suggested by Dundon and Henderson has been carried on in this work on the hydrates of nickel sulfate, and the method of application and calculation of data are made easier by the development of a simple formula. In this method is determined the weight of solvent which will bring a solution of unknown concentration to the concentration in which a glass float calibrated at an arbitrary temperature will remain in equilibrium.

Assuming the percentage of solid in equilibrium with a given solvent to be constant at a fixed temperature for a given float, the weight of solute in an unknown solution can be found by bringing the solution to the same density as the calibrated float at the calibration temperature and then multiplying the weight of the resulting equilibrium solution by that factor which has been determined from the calibration of the float. From the weight of the original solution, the weight of the solvent added, and the factor for the float, the concentration for the unknown solution can be easily calculated.

The actual density of the float, whether greater or less than that of the solutions to be studied, does not materially affect the calculations. When the density of the float is less than the solutions to be analyzed, solvent will always necessarily be added to the unknown samples to bring them to the density of the float. If the density of the float is greater than that of the solution to be analyzed, it becomes necessary to evaporate the solvent from the solution until it and the float are in equilibrium. The value for solvent added then becomes a negative value instead of a positive one, as in the case above.

The purpose of the work herein described is to study the applicability of the floating equilibrium method (1) to the analysis of the concentration of solutions of nickel sulfate, and (2) to the determination of the solubility of the various hydrates of nickel sulfate.

Preparation of the Pure Salt

A large quantity of the best grade of C. P. nickel sulfate was recrystallized from distilled water three times, this

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[1] Received March 28, 1923.

[2] *J. Am. Chem. Soc.*, **34**, 599 (1912); **36**, 1 (1914).

[3] *Ibid.*, **35**, 1666 (1913).

[4] *Ibid.*, **44**, 1197 (1922).

material alone being used for stock in the determinations, no residues from the determinations being used over again. The stock salt was the pale green, rhombic crystals of the formula $NiSO_4.7H_2O$. Tests for impurities showed no iron or hydrogen sulfide metals, and but minute traces of chloride and cobalt. The three hydrates of nickel sulfate were made by recrystallization of the stock sulfate at 25° C. for the heptahydrate (green), 40° C. for the hexahydrate (blue), and 70° C. for the hexahydrate (green). By carefully maintaining the temperatures until crystallization set in, then rapidly swinging off the mother liquor, a fine, stable grade of each of the hydrates was obtained, which underwent no noticeable change in color or hydration on standing in stoppered bottles. Analysis of the crystals for nickel by the dimethylglyoxime method proved their purity and formula as to nickel content. On the stock nickel sulfate heptahydrate the percentages of nickel were calculated from the analyses as 20.42, 20.90, 20.85. Calculation of the same from the formula gives 20.89 per cent. Analyses of the blue monoclinic and green hexahydrate for nickel content gave 22.42, 22.30, and 22.31 per cent while the theoretical quantity present should be 22.326 per cent.

A hollow, pear-shaped glass float, with a fine capillary at one end, occupying, a volume of about 1.5 to 2.0 cc. was made from ordinary, small, soft-glass test tubes. A solution of nickel sulfate approximately saturated at 0° C. was prepared, and by the addition of mercury through the capillary the float was brought to about the same density as the solution at room temperature. The capillary was then sealed off. The float used in these determinations was made about four weeks before the calibration, thus avoiding any large error due to slow contraction of the glass on aging. A subsequent calibration at the conclusion of the solubility determinations showed that no perceptible change in volume had taken place after the first calibration.

The determination of the exact concentration of the solution having the same density as the float was conducted as follows: A solution of nickel sulfate saturated at room temperature or below was placed in an 8-inch test tube with the glass stirrer and float. This apparatus was then put into the thermostat regulated at 25° C. Water was then added with constant stirring until floating equilibrium—that condition of the float when it remains suspended, or nearly so, in the body of the liquid—was reached.

Samples of five different solutions of nickel sulfate brought to the same density as that of the float at 25° C. and analyzed for nickel by the dimethylglyoxime method,[5] gave the following results in grams nickel sulfate (anhydrous) per gram of water: 0.30259, 0.30755, 0.30686, 0.30304, and 0.30250. The mean of these five values—viz., 0.30451—is taken as the weight of anhydrous nickel sulfate which when dissolved in 1 gram of water gives a solution with a density equal to that of the float at 25.00° C.

APPARATUS AND METHOD

A 40-liter thermostat was regulated at 25° C. to within 0.01 degree by a large toluene regulator. In this thermostat the solutions were maintained at the same floating equilibrium temperature at which the float was calibrated. A 10-liter thermostat, fitted up with a heating unit and relay regulated to maintain any temperature to within 0.01 degree by a toluene regulator and stirring device, was used for saturating solutions at a definite temperature. The agitators for the saturation flask were motor-driven. The thermometers used were carefully calibrated.

The solubilities of the various hydrates were determined by enclosing an excess of the hydrate with boiled distilled water in a 250-cc. flask fitted with a rubber stopper through which passed a stirring device driven by an electric motor. This apparatus was immersed in the 10-liter thermostat regulated at first at a temperature 2 or 3 degrees above the temperature at which a saturated solution was desired. Preliminary experiments having shown that equilibrium was reached in about 12 hours, the solutions were stirred for that time to insure saturation. The temperature was then dropped to the desired temperature and held at this point for 12 hours.

When it was desired to filter the solution, a piece of glass tubing with a small bulb blown near the end, the bulb packed with cotton and glass wool to serve as a filter, was substituted for the stirrer. The other end of the tube passed into a clean, dried tube, in which the solution was to be weighed. The solubility flask was also fitted with a suction tube, and by applying suction the solution was filtered and withdrawn from the flask into the solubility tube without having been for an instant removed from the bath.

In making the determination, the stoppered test tube into which the sample was drawn was first weighed with the glass stirrer and calibrated float. After the sample had been drawn into this apparatus at the proper temperature, the tube with its stopper, stirrer, float, and solution were reweighed—proper drying and temperature precautions having been taken. To this arrangement in the 25° C. bath, water was added from a buret with stirring until floating equilibrium was reached. The end point was that point at which the float would remain suspended in the solution. If the end point was passed, air was blown gently over the solution until sufficient evaporation took place to cause the float to rise, when water was again added to reach the end point.

It was possible by this means to determine the concentration of a solution of nickel sulfate saturated at any temperature by determining the amount of water required to bring the solution to the same density as the float. The weight of water added to or evaporated from the body of the saturated liquid previously weighed, was a measure of the concentration of the original solution, and the weight of nickel sulfate per gram of water was calculated as follows:

Let G equal the weight of nickel sulfate per gram of water at 25° C., and W_1 the weight of 1 cc. of water. Then G/W_1 equals concentration of standard solution at 25° C. At another temperature and condition of saturation, let x equal number of grams of nickel sulfate dissolved in W_2 grams of water, or the concentration of the solution equals x/W_2. If total weight of solution is A, then $W_2 = A - x$. x/W_2 may be made equal to G/W_1 by adding more solvent to or allowing evaporation from the solution x/W_2 until floating equilibrium is attained with the float. W_3 is weight of water added to or allowed to evaporate from the solution.

$$\text{Therefore} \qquad \frac{x}{W_2 + W_3} = \frac{G}{W_1}$$

$$\text{Since} \qquad W_2 = (A - x)$$

$$\text{Then} \qquad \frac{G}{W_1} = \frac{x}{(A - x) + W_3}$$

$$\text{Or} \qquad x = \frac{G}{W_1 + G}(A + W_3)$$

To determine the concentration of the solution in terms of anhydrous nickel sulfate per 100 grams solvent, the formula becomes:

$$Y = \frac{100x}{W_2} \text{ or } \frac{100x}{(A - x)}$$

Substituting in the values for x:

$$Y = \frac{100 \dfrac{G_1}{W_1 + G_1}(A + W_3)}{A - \dfrac{G_1}{W_1 + G_1}(A + W_3)}$$

Since the calibration of the float determines the value of G and W_1, the calculation of results resolves itself into substituting in the above formula the value for $\dfrac{G}{W_1 + G_1}$, which, when once determined for the float, becomes constant, and also the values of the weight of the solution analyzed, A, and the weight, W_3, of the solvent added or evaporated from the solution. If the float is too heavy for the solution and the solvent must be evaporated from the solution, the value of W_3 takes on the negative sign.

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[5] Griffin, "Technical Methods of Analysis," McGraw-Hill Co., New York, 1921, p. 121.

According to the calibration results, $\frac{G}{W_1} = 0.30451$; therefore $\frac{G}{W_1 + G}$ is equal to 0.2334. The formula for determining the concentration of unknown solutions then becomes:

$$Y = \frac{100\,(0.2334)(A + W_3)}{A - 0.2334\,(A + W_3)}$$

A test of the accuracy of the method as compared with results obtained gravimetrically for the determination of nickel by the glyoxime method showed concordance. The results in terms of grams of anhydrous nickel sulfate per 100 grams solvent were as follows:

Floating equilibrium method.......	30.304	30.250	30.292
Gravimetric method..............	30.296	30.178	30.284

Discussion of Results

The data obtained on the solubility of the various hydrates of nickel sulfate are given in Table I. All weighings have been reduced to the vacuum basis. Comparison is shown between the float and gravimetric results. The gravimetric analyses are averages of three determinations.

Table I—Solubilities of Hydrates of Nickel Sulfate

Temp. ° C.	Weight of Solution A	Weight of Solution + Added Solvent $A + W_3$	Grams $NiSO_4$ (Anhydrous) per 100 G. Water Float	Gravimetric	Type of Salt
−4.25	136.8331	124.9331	27.335	27.187	$NiSO_4.7H_2O$ (Green)
−2.00	146.3774	118.7795	23.366	23.543	
0.00	35.5239	31.6771	26.189	26.087	
3.19	125.2792	120.2928	28.884	28.765	
6.00(*a*)	145.4360	145.3731	30.304	30.253	
(*b*)	108.8146	108.6617	30.250	....	
(*c*)	110.4139	110.2466	30.292	....	
15.65	112.3565	126.0980	35.491	35.124	
25.00(*a*)	107.2881	132.4285	40.469	40.417	
(*b*)	101.7064	126.0940	40.720	....	
30.00(*a*)	109.1731	142.2885	43.719	43.289	
(*b*)	105.3053	136.8687	43.546	....	
(*c*)	107.6976	139.7399	43.439	....	
31.71	107.0614	142.9922	45.299	45.187	$NiSO_4.6H_2O$ (Blue)
40.00(*a*)	121.3861	167.0780	47.329	47.437	
(*b*)	67.0706	92.8400	47.727	....	
50.00(*a*)	102.3786	150.5640	52.267	52.291	
(*b*)	110.2000	161.7555	52.075	....	
53.25	105.1427	158.0395	54.041	54.009	
58.21	104.1877	159.1173	55.389	55.177	$NiSO_4.6H_2O$ (Green)
60.11	103.4108	158.2371	55.557	55.396	
79.75	96.9927	162.9067	64.476	64 217	
94.22	136.3227	245.6684	72.597	72.424	

In checking with the gravimetric method, the results obtained indicate the applicability of the float method. If it is assumed that the density under standard conditions is a true measure of concentration, then the accuracy of the method depends upon temperature control and the weighings. The weighing of large samples for analysis obviates a painstaking care in the analysis by reducing the effect of small errors in weighing and procedure. Several drops of liquid excess will not influence the final results on such large samples, but the sensitivity of the float does not permit of a variation over one drop, since only one drop makes a decided difference in concentration. Ordinary precautions as to determinations of densities by float hydrometers apply equally well here.

The time required for making an analysis is indeed very small when compared with the long gravimetric methods for determining the concentration of constituents present.

The ordinary floating hydrometer type with an exposed stem protruding through the surface of the liquid can be used, but the sensitivity is not very great owing to the variation in the surface tension on the exposed stem. One drop of water on a float in equilibrium will cause a sinking, while the effect on an hydrometer float would be negligible. The floating equilibrium method in analyzing solutions for concentration is therefore more accurate than the hydrometer gravity determinations.

The values plotted on a curve (Fig. 1) show a comparison with those obtained by gravimetric analysis by Steele and Jackson.[6] The values obtained by the float method are slightly higher than these, but this may be due to the difference in values obtained for the components owing to the different methods of analysis used. The float method agrees well with the gravimetric methods made in our own work, the float having been calibrated by the same method as used for the gravimetric data.

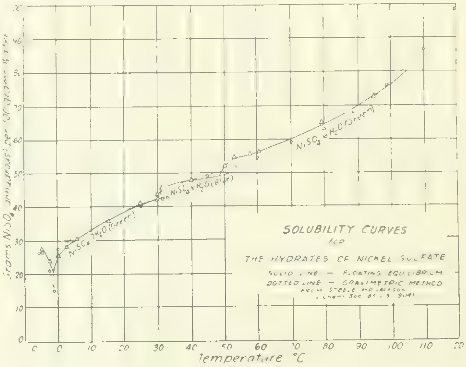

Fig. 1

The possibilities of the application of the principle of floating equilibrium are very great. Where great accuracy is desired and neither time nor opportunity for making a gravimetric analysis is possible, this method suggests itself. Also, in the analysis for concentrations of solutions such as unstable organic compounds, which require exceedingly great care in analysis because of the unstableness or other difficulties encountered, the float method recommends itself, for when a float is once calibrated for the given solvent and solute, concentrations are easily determined.

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[6] *J. Chem. Soc.* (*London*), **85**, 113 (1904).

A Remedy in Sight

On several occasions we have called attention to the practice of certain so-called American universities who have offered academic degrees for sale. This campaign has had no success in America, but unfortunately attracted certain individuals in foreign countries much to the embarrassment of America.

A recent announcement gives reason for hope that the charter given in good faith by a state legislature and officially purchased by the principal offender in marketing degrees may be revoked. The spurious university in question has been cited to show cause why its charter should not be revoked. It is our earnest hope that it may be speedily revoked and this pernicious practice made impossible in future.

Earning Power of Research

Recently, a corporation capitalized at a very substantial figure closed its plants, dismissed its sales force, and practically retired from business. This failure is mainly attributable to the fact that a competitor succeeded in winning and holding certain foreign trade. The successful concern was able to do this because years ago he turned to research and scientific control, whereas the unsuccessful concern, tardy in its recognition of science, was unfortunate in the selection of its scientific personnel, in the choice of its problems, and perhaps did not adequately support a scientific program. It is another instance of the difference between success and failure, success resting with science.

The Work of the Color Laboratory[1,2]

By Joseph A. Ambler[3]

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

THE original aims of the Color Laboratory and problems first studied by it have been described by Gibbs.[4] At the time of the publication of these statements, the principal question confronting the dye industry may be briefly stated as one of tonnage. Because of the demand for large amounts of dyestuffs, it was possible to produce and sell at a profit, dyes which were made by very crude and inefficient processes. The dye industry has now passed into a second stage of development wherein, to a large extent, the question of tonnage has been solved. The problems at present confronting dye manufacturers are those of quality of the dye and efficiency of the processes. The work of the Color Laboratory, therefore, has been directed for some time along those lines which would help the manufacturer in acquiring suitable control of the processes used so that the quality and the yield of the dyes may be improved. It is felt that this might be accomplished by undertaking exhaustive studies on the chemical and physical properties and general reactions of the crudes, intermediates, and dyes, and by endeavoring to devise more refined methods of analysis, which would make it possible to follow more closely the course of reactions involved in dye chemistry. Many problems of this nature are continually arising which have a bearing on the industry as a whole but which the manufacturer cannot afford to investigate, since he is forced to consider time and cost of production as paramount because of increasingly keen competition.

The results obtained from all studies undertaken are the property of the people of the United States and are made available to all by publication. For this reason it is not permissible to undertake problems which benefit one concern only, with the possible creation of a monopoly through the securing by that concern of patent rights. The investigation of problems of this character is the duty of the consulting chemists of the company, not that of a government laboratory supported by taxes derived from the people.

Another important function of the Color Laboratory relates to a type of problem which has been undertaken in the past, and which will again be handled in the future, should occasion arise. There are certain dyes which have very limited use, but which are of the utmost importance in special lines of work by which the welfare of the public is bettered or protected. It has happened occasionally that dyes of this sort were not manufactured, or were not obtainable, in this country. Under such circumstances the Color Laboratory will study the production of the dye in question and produce it for investigators until such a time as some manufacturer places it upon the market. The sale of such material cannot be continued indefinitely, however, since the laboratory can sell such products only when they originate as the result of research work and are of no further use to the Government. Such a case was that of the photosensitizing dyes, which were investigated, produced, and sold by the Color Laboratory only until it was possible for a manufacturer to supply them. When a problem of this character is undertaken, it is not with the intent of competing in any way with the manufacturers. This function of the Color Laboratory is not competitive, but stimulative. Such problems are attacked with the purpose of developing a process for the production of the dye which shall be simple enough to make it possible to interest a manufacturer in producing it for the trade. All the data acquired in the study of the process are placed at the disposal of the interested manufacturer, and are eventually published.

Problems of the nature discussed above are frequently encountered in the industry, and, if communicated to the Color Laboratory, will be undertaken as speedily as possible. The service which the laboratory can render the industry will be greatly increased by the suggestion of such problems, and coöperation of this type will be helpful to all.

Besides investigation work, there is a function of the Color Laboratory which is regulatory and routine in character and which was the original reason for the establishment of this laboratory in the Department of Agriculture. This work originated as a consequence of the passage of the Food and Drugs Act in 1906, and deals with the coal-tar colors for use in foods. The chemical work necessary to ascertain which coal-tar dyes are noninjurious, and, when pure, are fit for use in foods, is carried on by this laboratory. At present there are only eleven dyes of this character. These are known as the permitted food colors and the use of any other coal-tar dye for food purposes is prohibited. A system of certification of these dyes, and mixtures of them,[5] has been devised whereby each batch of food color manufactured is examined, and if found of satisfactory purity is assigned a number which amounts to a guarantee that the product has met the specifications of the department for this class of colors. During the fiscal year ending June 30, 1922, there were certified 333,330 pounds of coal-tar colors for food purposes. The amount of coal-tar colors certified is steadily increasing. This does not necessarily mean that more artificial color is being used in food, but should be interpreted rather as an indication that the manufacturers of food products are coming to realize the necessity of employing high-grade and noninjurious colors for their products and are demanding the certified colors in increasingly large amounts. The use of ordinary textile coal-tar dyes in foods may be attended with considerable danger to the health of the consumer.

It is well known that textile dyes, including also the textile grades of the permitted dyes, are very seldom carefully purified and often contain relatively large amounts of arsenic, uncombined intermediates, and poisonous substances derived from the apparatus and materials used in their manufacture. When such impurities are introduced into food with the coloring matter, the resulting food product may be deemed adulterated under the terms of the Food and Drugs Act.

Brief statements follow concerning several problems which are of special interest and concerning which very little has been published.

COÖPERATION ON THE STANDARDIZATION OF BIOLOGICAL STAINS

Before the war the dyes used for biological stains were supplied exclusively by Germany. These German stains were considered by the biologists as standard products and the only ones suitable

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[1] Presented before the Division of Dye Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Contribution No. 79 from the Color Laboratory, Bureau of Chemistry, Washington, D. C.

[3] Chemist in Charge.

[4] THIS JOURNAL, **10**, 802 (1918); *Chem. Met. Eng.*, **22**, 405 (1920).

[5] Details of the procedure for certification may be obtained by writing to the Bureau of Chemistry, Department of Agriculture.

for their work. This state of affairs is exactly analogous to that which obtained in the textile industries at the time that German dyes were shut off from this country. The American manufacturers were attempting to produce products suitable for staining, but in many cases the biologists found that these products were unsatisfactory. Therefore, work was started to examine the American stains and to draw up specifications to which dyes for this purpose must conform. The chemical work which this entails is being performed in the Color Laboratory. In the case of every dye used as a stain which has been examined chemically, it has been found that the American stains are superior to the German in their purity and strength of color and that there are American stains obtainable which are as good as or superior to the pre-war material in their staining qualities. Apparently, however, chemical purity and color strength alone are not the final criteria for a satisfactory biological stain. The biologists have awakened to this fact, and realize now as never before that a large amount of fundamental research on staining operations is necessary in order that this important phase of their work may be based upon a secure scientific foundation.

UTILIZATION OF FURFURAL

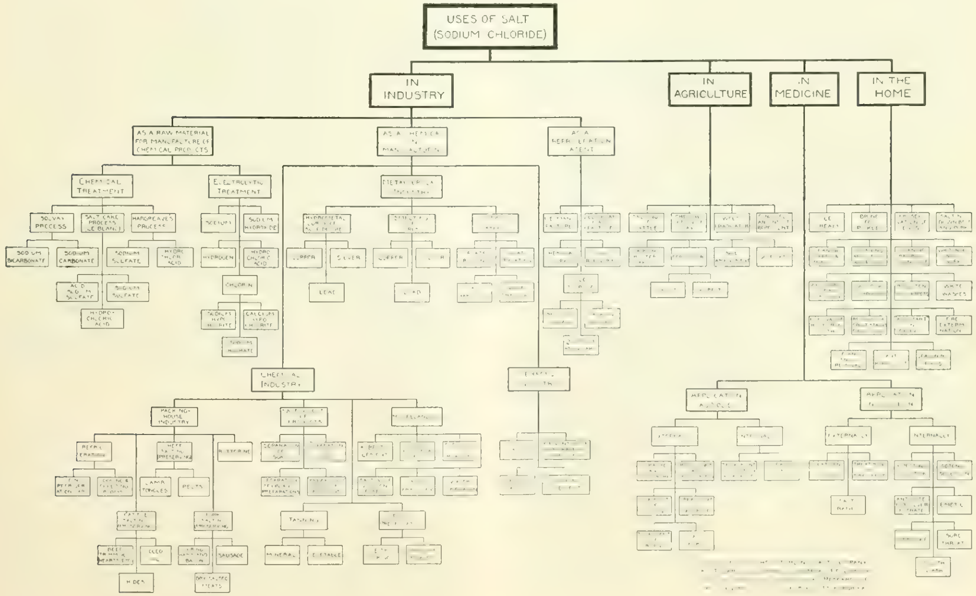
When it became evident some little time ago that it was possible to produce furfural in considerable quantities from corncobs and other agricultural wastes, the question arose as to whether this interesting compound could be used to advantage in the dye industry. Several dyes of representative types were prepared. Those of the triphenylmethane group, wherein the furfural was used as a substitute for benzaldehyde, proved to be extremely fugitive to light. In fact, the only dyes which were not fugitive were yellow and brown sulfur dyes, which had no superiority over well-known dyes of similar shade. When it was shown that furfural was not suitable as an intermediate for dyes, the problem resolved itself into one of finding another field wherein furfural could be used to advantage. At present the most promising uses of this compound seem to be: (1) for the production of phenol condensation products of the type of Bakelite and Redmanol wherein the furfural is used in place of formaldehyde; (2) for the production of resins by condensation with amines, thereby producing soluble resins which may possibly have a use in the paint and varnish industry; and (3) for the preparation of paint and varnish removers wherein the peculiar solvent properties of this compound are utilized.

SYNTHETIC THYMOL

In the sulfite paper pulp process there is produced as a byproduct a considerable quantity of *p*-cymene or "spruce turpentine." One million gallons of this hydrocarbon are allowed to go to waste each year in the United States. There has been developed in this laboratory a process for the production of thymol from this material, and an endeavor is being made to test out the process for the production of this valuable anthelmintic on a large scale. The reactions employed are those commonly used in dye chemistry, such as sulfonation, nitration, reduction, diazotization, and alkali fusions. A public service patent dedicated to the people of the United States for their free use has been obtained for this process.

PUBLICATIONS OF THE COLOR LABORATORY

Reports of the results obtained with other problems investigated in this laboratory have been published from time to time and a list of these publications may be obtained upon application to the author.



The Appraisal of Chemical Invention[1]

By **D. B. Keyes**

U. S. Industrial Alcohol Co., New York, N. Y.

INVENTORS do not have an easy time when they undertake to sell their inventions to a corporation. The inventor can appraise his process as easily and as accurately as the corporation, once he understands the principles of such an analysis, and this appraisal would be of great help to him in his work. It has been the writer's privilege to investigate a great many chemical inventions, and ideas developed by this experience may be of interest to the reader.

The new process is a financial gamble, no matter how glorious its future may seem to the inventor. The agent of capital confines his investigation to two fundamental questions—what is the financial risk, and what is the probable financial return?

Patent Situation

The corporation buys not only an idea, but also protection for the idea. An idea that any competitor may appropriate later and use is of very little value. The only legal monopoly recognized by the United States is a patent monopoly. The inventor should have a strong patent situation to sell as well as his process.

A patent protects the inventor against the unscrupulous manufacturer who wishes to appropriate the idea; and a patent also protects the corporation against the unjust claims of a misguided inventor who believes he has been robbed. It is much more satisfactory for both sides to have the invention patented. The appraisal of a patent, as indicated below, will give in itself a fairly clear idea of the value of the process.

Many things must be looked for in a patent situation, but only the common weak points will be described here. Often the patent lawyer who drew up the patent application knew no chemistry and the inventor knew no patent law—a disastrous combination. The patent claims may be too narrow. Very few inventors realize at once the full meaning of their invention, and the extent of its application. Broad and accurate patent claims are the result of extensive research work and thought. There are many ways in which the patent claims can be narrow, two of which are very common. The first is the long claim which is full of detailed description. Value and length of claims vary with the inverse ratio of one another. The second common fault is the failure to claim the use of chemical types in a process in contrast to specific chemicals. In a patent on a process using chlorine it would be well to claim the use of halogens, providing they would work. In case the chlorine was used as an oxidizer, other oxidizing agents should be tried, and if they also work claims covering oxidizing agents should be added. Misstatements should be looked for in the patent specification, because they may render the patent invalid. Misstatements in theory are not important, but misstatements in fact caused by careless research work or lack of understanding between lawyer and inventor are fatal. No essential detail should be concealed. Several well-known United States patents taken out by foreigners have proved to be valueless because important features were left out; the inventors expected to cheat the public and at the same time keep their monopoly. Ample ranges of temperature, concentration, and pressure must be specified, otherwise a competitor may get a foothold and seize profits that do not belong to him. Care must be taken not to claim too much, as it is sometimes found that the example worked out is an exception and not one of a series. Some lawyers try to crowd into a few claims the entire invention, but it is a very narrow invention that can be treated adequately in this manner. The patent or patents should contain a clear statement of just what the inventor has produced, and the form should be in accordance with good patent law practice.

The general patent situation must be examined as well as the patent. A patent may be valid and cover accurately a worthwhile invention and still be of little value. It may be an improvement on a process patented by someone else. A valid patent owned by one oil company, covering an improvement on the cracking process owned and patented by another oil company, cannot be used by the former without the permission of the latter. It is also true that the second company cannot use this improvement, but it can operate its own and probably can acquire the improvement for a comparatively small sum. A thorough literature search will disclose this condition.

Another case that frequently occurs. The inventor has a valid basic patent covering his process, but his process is dependent upon a raw material whose process of manufacture is covered by a patent controlled by some one else. The inventor has two choices—he can either invent a new and better process of manufacture of this raw material, or he can come to some agreement with the owner of the patent. If he does nothing the value of his invention is small. In Canada at present, one concern controls the patents on the practical means of synthesizing acetaldehyde. It would be unwise for another Canadian concern to pay a large sum for a process involving the use of large amounts of acetaldehyde before finding out what arrangements could be made with the manufacturers of this uncommon raw material. Quite often the sole manufacturer of a patent-protected chemical is very fair and sensible, showing no tendency to gouge the buyer, but this is not always the case.

Another type of a weak patent situation is common. The inventor has produced a chemical for which there is only one buyer.

The Process

The economics of the process is of course as important as the patent situation.

Raw Material—The raw material should be cheap and standard in price. Chemicals made from caustic alkali, sulfuric acid, alcohol, etc., find more favor with the chemical manufacturers than chemicals made from phenyl hydrazine, ethylene glycol, diacetone alcohol, etc. The same argument applies to raw materials that are constantly varying in price. Even such stable commodities as corn vary so much in price that at times acetone and butyl alcohol, which are made from this material, are not very profitable. The raw material must be easily available and not widely scattered.

Yields—Yields or efficiency figures should be scrutinized with great care in order to find out exactly what they signify. Conversion factors and over-all yields should be clearly differentiated. The former is not necessarily important, as a low factor may signify that the remainder goes through untouched and can be sent through again at a very small cost. Figures should be given based on the most costly raw material. In fact, the yields must be calculated on each raw material in order to estimate the total cost. A large allowance for possible inaccuracy in yields should be made in every case.

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[1] Received April 28, 1923.

APPARATUS—The inventor should be in a position to show the process in operation, but not necessarily on a commercial scale. The strongest sales argument possible is a working successful process. The corporation agent wants to see the facts with his own eyes. He wants to take his own data and possibly operate the process himself. Some apparatus just beyond the laboratory scale is all that is necessary to convince one of the probable yields and to give a fair idea of costs. Data showing yields of previous similar processes are worth having. The time necessary for the whole operation should be considered. It is difficult to predict the performance of large-scale, standard apparatus using a new process from laboratory results, and it is impossible to predict what a new and novel apparatus is going to do when enlarged appreciably. The new invention approaches perfection from the practical standpoint if the separate steps are well known and can be carried out in standard apparatus.

One of the best ways to consider the practicability of a process and an apparatus is to consider them from the operator's viewpoint. Picture each operation in the mind and look for trouble. The general manager of a plant once insisted that a fractionating column should be cut in two parts because it seemed so tall that repairs would be difficult. The column was built as he directed and the first repairs were made on the bottom plate of the bottom section. His opinion was justified. Complicated and delicate apparatus should never be connected directly with a crude, rough-going apparatus; the delicate mechanism will soon be thrown out of operation. The apparatus should have "universal joints" or reservoirs between separate operations in order to take up temporary "slack." Low-speed machines are usually preferable to those of high speed.

The great question of whether to use men or machinery is very complicated. It is best to start with men and slowly replace them with thoroughly tested machinery. Unfortunately, there is little literature at present that will guide one in the proper selection of chemical apparatus. Experience alone must be relied on when it comes to criticizing an apparatus layout.

BY-PRODUCTS AND MATERIALS—By-products should be closely scrutinized, not only for their market conditions or commercial value, but also for the cost of disposal if they are valueless. State laws concerning industrial waste disposal are growing more numerous and more rigid, and the subject is attracting national interest.

Inside the plant the by-products, or the materials in operation, may cause trouble due to a corrosive, or highly poisonous character. Trouble means added cost. The men operating a phosgene plant must be paid more than those operating a rock crusher. In a dyeing operation an attempt was made to replace acetic acid with formic acid; it failed because of the added cost of handling the formic acid.

Any material in the process that has a tendency to gum up the operation and break up the continuity should be carefully considered, because shutdowns, delays, and repairs often cost much more than raw materials. A certain process required the multiple effect evaporation of a sirup. The evaporators would run continuously for sixteen hours on this material and then had to be shut down for cleaning. The cleaning required five or six hours. This time should be added to the sixteen hours in any cost calculations.

PRODUCT

In considering the product, the first question is whether it is old or new. If the product is old and standard, the estimation of its probable market is much simpler than if the product is new and unique. The sales promotion and development of a new chemical is a costly and hazardous undertaking. Advertising applied to chemicals is still in a very crude state—one needs only to glance over the pages of a chemical trade journal to appreciate this fact. It is not unusual to find that a new chemical product was visualized or invented in ten minutes, that it took ten months to put it on a production scale, and ten years to obtain a satisfactory market for it. Ethyl acetoacetate has been known to chemists for fifty years; about three years ago a new and better method was invented for its manufacture; a year later it was manufactured for the first time in a semicommercial unit in this country; but it was only recently that this well-known chemical found a real market here. The inventor who has a process for the synthesis of glycerol will receive more attention than the inventor of a process for the synthesis of ethylene glycol.

The specifications of the product are often vital, a fraction of one per cent of certain impurities may cut the value of the product in half. Ethyl alcohol free from water is entirely different in its properties from a 96 per cent ethyl alcohol. A small percentage of sodium or potassium in metallic magnesium ruins the latter's resistance to corrosion. Cases also occur in which the so-called impurity has been found to be absolutely necessary; alloys are good illustrations.

Some products sell well only during certain seasons of the year. This means added cost of storage and investment, and should be carefully investigated. Market conditions for the particular product may show a definite trend. Production figures and prices over several years should be known.

More consideration is necessary if the probable competitor's chief product is this chemical, than if this chemical is only one product among many manufactured by the competitor. The question is—what resistance will there be to the corporation's entry into the field? The manufacturers of potash in America have found out how much the foreign producers valued the American market, and the lengths they would go to keep it.

Before approaching a corporation an inventor should know the corporation's field of activity. There is small chance of the corporation taking up some invention that is only remotely connected with its business. Transportation requirements for the particular chemical are of interest. Inflammable liquids, poisons, and very valuable materials, for example, have their special transportation costs.

Oftentimes the product is subject to specific laws and regulations. This red tape means added cost. The manufacturer of industrial alcohol is subjected to every indignity known to man and the customer must pay for this foolishness, even though alcohol is one of the three greatest raw materials used in the chemical industry.

The Bureau of Foreign and Domestic Commerce announces the appointment of Ralph H. Ackerman as commercial attaché at Santiago, Chile. Mr. Ackerman, who has been chief of the Latin-American Division of the bureau for nearly two years, is planning to leave Washington for his new post about September 1. Mr. Ackerman has been closely associated with Latin-American trade for many years. He was for some time a representative in Argentina of the Southern Railroad System, and later represented numerous manufacturers in Buenos Aires. Subsequent to this he had wide experience as manager of export commission houses in New York and Philadelphia. His extensive knowledge of the Latin-American republics and of the trade problems presented by them has been gained through long residence in those countries and close association with their people.

The personnel of the field expedition that is to investigate rubber possibilities in the Philippines, in behalf of the Department of Commerce, is as follows:

C. F. Vance, of Troy, Ohio, Special Agent, is in charge of the expedition. Mr. Vance has had fifteen years' experience in the Philippines and is thoroughly conversant with the small rubber plantation situation in the islands. Mr. Vance will be assisted by Alex H. Muzzal, of Carpinteria, Calif., a practical rubber plantation man who has for many years been connected with the Goodyear plantations in Sumatra; by John P. Bushnell, of Washington, D. C., Assistant Trade Commissioner of the Department of Commerce, who has been connected with rubber investigation activities of the department since its inception; and by Mark Baldwin of the Bureau of Soils, Department of Agriculture

AMERICAN CONTEMPORARIES

Edward Hart

In 1874 there came to Lafayette College as professor of analytical chemistry, Thomas M. Drown, later president of Lehigh University. With him there came as his assistant a young Quaker from Doylestown, Pa., by the name of Edward Hart. According to his own report, he was as verdant as any of the freshmen and he was immediately christened into the collegiate family as "Buddy," and Buddy Hart he still remains after fifty years, although the tints of the spring of life have changed to those of autumn. As an indication of his virility, his versatility, and even of his friendliness, the nickname was very happily chosen.

Alman & Co.
EDWARD HART

Under his great teacher he certainly sprouted out in a variety of directions. Not satisfied with his knowledge of organic chemistry, in 1876 he applied for a fellowship at the newly started Johns Hopkins University. Dr. Remsen must have scanned young Hart more carefully than he did his college diploma, for the latter was nonexistent; but however that may be, Edward Hart was given the fellowship and he kept it for two years and received his doctorate into the bargain.

This was in 1879, but John Wiley had published his first book, entitled a "Handbook of Volumetric Analysis," in 1878. His first paper was published in the *American Chemist* in 1875, a second appeared in the same journal in 1876, and one appeared in the *Chemical News* in the same year. Dr. Drown resigned in 1881 and Dr. Hart was then made assistant professor in charge of the department, with the magnificent salary of $1200. As a possible explanation of the size of his salary, it must be recalled that Dr. Hart was without his collegiate degree and this constituted a certain defect in the eyes of President Cattell. This defect in Dr. Hart was fortunately not entirely irremediable, so the college gave him the anomalous degree of honorary bachelor of science. Thus, he is an alumnus without any classmates—a sort of B.S. Extraordinary!

It was at this time that President Tuttle of Wabash College offered him a professorship, which he considered seriously. When it became noised abroad that he was considering a change of base, President Cattell came to him with an offer of preferment, both in rank and income, which he could quite conscientiously do now that Dr. Hart had his collegiate degree.

Another reason for remaining in Easton was that Dr. Hart had already started a series of business enterprises which were to assist in supporting his rapidly growing family—he has had eight children. In 1881, with John T. Baker, a Lafayette graduate of 1878, he began to make refined chemicals. They were without experience and with only $500 capital, but they possessed plenty of courage. Renting land at $10 per year, they put up rough buildings, erected furnaces, and started in to manufacture pure hydrochloric acid, nitric acid, sulfuric acid, and ammonium hydroxide. After two years their capital proved too small and they took in George P. Adamson, of the class of 1884, and moved the plant to a five-acre plot near the railroad. The use of crude nitric acid in considerable quantities suggested the manufacture of the acid directly from sodium nitrate, and this led to the invention of the Hart boiler and condenser, which are still widely used. Thus, with Dr. Hart as silent partner, the firm of Baker & Adamson was started, which was later merged into the General Chemical Company, and which in turn has merged into the Allied Chemical & Dye Corporation.

Dr. Hart very early took an interest in the art of the printer and used a small foot-power printing press in connection with his teaching. When he began to edit the *Journal of Analytical and Applied Chemistry* he found trouble in getting the journal out on time, so he audaciously decided to be his own printer and in 1887 he engaged a student as the foreman of the proposed company. In 1893 Harvey W. Wiley, who had recently become president of the AMERICAN CHEMICAL SOCIETY, requested Dr. Hart to become the editor of the journal. There thus started an intimate friendship which has increased with the passing years. Taking up the editorship, Dr. Hart found but two articles ahead while there were six numbers in arrears. He unselfishly gave up his *Journal of Analytical and Applied Chemistry* and merged it with the SOCIETY's journal. Dr. Wiley busied himself in getting papers, while Dr. Hart edited and printed them. In 1894 he published the first volume of Dr. Wiley's "Principles and Practice of Agricultural Analysis," and a year later Dr. Remsen asked to have the *American Chemical Journal* printed by the Chemical Publishing Company. From this company there later developed the Eschenbach Printing Company, which now prints all of the SOCIETY's journals as well as several other important technical publications. Dr. Hart gave up the editorship in 1901, but he has remained an associate editor of the *Journal of the American Chemical Society*.

The growth of the chemistry department of the college under Dr. Hart was continuous. From a few rooms in Pardee Hall, the department moved to a building of its own, Jenks Hall, which was soon outgrown. In 1902 a commodious new building was provided by James Gayley, himself a graduate of the department in the class of 1876 and a Perkin medalist. Mr. Gayley secured from Henry W. Oliver $5000 to endow the chemical library. In 1918 friends of Dr. Hart raised $10,000 to endow the Edward Hart Research Fellowship, as a tribute to his great service in building up chemistry in America. Although Dr. Hart retired from the direction of the chemistry department in 1916, he has retained the title of professor of chemical engineering and in a few months he will have completed a round fifty years of service as a teacher.

Dr. Hart possesses great originality together with boundless energy; but modesty in regard to his own attainments and kindliness are even more characteristic of his later years. Still working on important industrial problems, such as the recovery of potash from greensand, much of his time is given to civic work and to the improvement of the farm which he has recently developed. Dr. Hart's readings in old agricultural literature are perhaps the most extensive of any in the country. He is thoroughly acquainted with all the early authors, especially the

Latin and early English writers. His library is rich in this literature, and he has drawn a great inspiration therefrom, which is reflected in his little volume "My Farm in Cedar Valley." One may be a thorough theoretical chemist, a fine practical chemist, and an adept in chemical technology, and still retain the love of the fields and the forests.

To his friend, Harvey W. Wiley, we owe this intimate characterization:

> To my mind, Dr. Hart's personality is one of the most charming of the chemists that I have intimately known. It is always a joy to be with him and hear his discussions on chemistry and chemical technology.*** One of Dr. Hart's particular characteristics is his hospitality. He is the very genius of hospitality. It comes so evidently from the heart that one cannot fail to appreciate the privilege of being his guest. If he had devoted his whole time to manufacturing instead of to teaching he would certainly have been a millionaire. He has a remarkable instinct for technics and love of manufacturing. He is a very good business man in many other respects.*** One of the great charms of Dr. Hart is his conversational ability. I sit with him for hours and we discuss chemical and agricultural problems to my great delight.*** He is also a natural collector of antiques, especially in chemical literature, and gets a great deal of comfort by indulging this habit of seeking what is rare and difficult to find. Dr. Hart has a keen sense of humor, a very delightful memory of the men he has met in his chosen profession and of the impressions of travel which he has received.

Chemists spend so much time in laboratory and study that it is particularly pleasant to present evidence of generous public service. Dr. Hart was for two years a member of the Common Council of Easton and a member of the Highway Committee. He has been chairman of the Easton City Planning Commission since 1906. He has been three times president of the Northampton County Historical Society. He has been president of the Easton Motor Association, trustee of the Easton Board of Trade, and in 1912 he was candidate for Congress on the Progressive ticket. Although a practical printer, he advocates the use of the metric system in printing.

Along with his other work Dr. Hart has written several textbooks and considerable verse of a humorous or sentimental character. His description of "The Hobo" is certainly not autobiographical:

I think some evil molecules
  Must in my system lurk
I really am not lazy
  I just don't like to work.

EUGENE C. BINGHAM

Personals

John P. Harris, who for the past four years has been engaged in the practice of chemical engineering at Chicago and Kansas City, specializing on edible oil and packing house work, has been appointed director of the Bureau of Practical Research of the Institute of American Meat Packers, Chicago, Ill.

E. J. Casselman has resigned his position with the Westinghouse Electric & Manufacturing Company to accept a fellowship in ceramics at the Mellon Institute.

Leslie C. Beard, Jr., has resigned his position as instructor in chemistry at Johns Hopkins University to become a chemist for the Standard Oil Company of New York.

William W. Bray, who received the degree of master of science from the Massachusetts Institute of Technology in June, is now connected with the chemical division of the Procter & Gamble Co., Ivorydale, Ohio.

Carl Henlein, formerly in the color and dye research laboratories of the Ault & Wiborg Co., Cincinnati, Ohio, has taken charge of the Kentucky Color & Chemical Co., Louisville, Ky.

Raphael Rosen, fellow at Clark University and Ph.D., February, 1923, has joined the research staff of the Standard Oil Company of New York.

Earle G. McConnel resigned as chemist with the Knoxville Water Department, Knoxville, Tenn., to accept the position of superintendent of filtration with the Charlotte Water Works, Charlotte, N. C.

Luther T. Garey, who graduated from the University of Illinois in June, has accepted a position in the research laboratory of the Standard Oil Co., Whiting, Ind.

Charlotte L. Messler, who for the past two years has been in the employ of the A. O. Smith Corp., Milwaukee, Wis., has recently accepted a position with the Roessler & Hasslacher Chemical Co., Perth Amboy, N. J.

Aladar Jendrassik, a chemical engineer attached to the staff of the Polytechnical Institute of Budapest, has been inspecting the chemical laboratories in Washington.

Lawrence W. Trowbridge has resigned his position as chemical engineer in the laboratory of the Babcock & Wilcox Co., Bayonne, N. J., and has entered the employ of the International Engineering Works, Inc., Framingham, Mass.

E. B. Brown, who during the past two years has held the National Tuberculosis Association Fellowship in Organic Chemistry and Biochemistry at Yale University, has resigned to accept a position as research chemist in the Fleischmann Laboratories.

I. K. Phelps, formerly of the Bureau of Chemistry, is now engaged in research and development work for the Wamesit Chemical Company of Lowell and Wamesit, Mass.

Sidney H. Keoughan has been elected chairman of the board of directors of the Mutual Oil Co., Denver, Colo., operating oil refineries. He was formerly vice president of the company.

Francis B. Davis, Jr., for some years an employee of the du Pont Company, has been made general manager of the Pyralin Department. **R. W. Brokaw** has been advanced to the position of assistant general manager.

F. C. Binnall has resigned his position with the United Light & Railways Company to accept an appointment as research and combustion engineer with the Standard Sanitary Manufacturing Co., Pittsburgh, Pa.

B. H. Knight and **John Clarke,** who were for several years associated with the late Parker C. McIlhiney, and who were in entire charge of his business during the long illness which preceded his death, have formed a partnership to continue the practice of analytical and consulting chemistry at 50 East 41st St., New York City. In accordance with Doctor McIlhiney's wishes, his laboratory has been turned over by his estate to Messrs. Knight and Clarke.

E. H. Darby, assistant professor of chemistry at Union College, has resigned to accept a position as director of the research laboratories of the Rome Wire Co., Rome, N. Y.

Lowell H. Milligan, who received the degree of doctor of philosophy in chemistry and physics in June at Cornell University, has taken a position as research chemist with the Norton Co., Worcester, Mass.

H. J. Knollman, formerly ceramic engineer with the Abrasive Co., Philadelphia, is now employed as ceramic engineer and chemist with the Pacific Clay Products Co. at Los Angeles, Calif.

W. A. McKnight, formerly connected with the Aluminum Company of America, has accepted the position of vice president and general manager of William F. Jobbins, Inc.

W. M. Weigel, formerly stationed at the Southern Station of the Bureau of Mines, Tuscaloosa, Ala., has been transferred to the Washington office and will succeed Oliver Bowles as mineral technologist.

F. W. Zerban, at present research chemist with Pennick & Ford, Marrero, La., will succeed Charles A. Browne as chemist in charge of the New York Sugar Trade Laboratory, New York City.

R. Norris Shreve, W. Schmidtmann, and **W. P. TenEyck** have organized the Ammonite Company in New York for the manufacture of ammonium salts.

Edwin S. Cavett has resigned from the employ of the American Leather Oak Co., Cincinnati, Ohio, to engage in research on the tanning of sole leather with E. C. Smoot & Sons, North Wilkesboro, N. C.

International Union of Pure and Applied Chemistry

The International Union of Pure and Applied Chemistry held its fourth annual meeting in Cambridge, England, June 17 to 20, 1923, under the presidency of Sir William Pope. The meeting was attended by delegates from twenty-one countries and was one of the most successful meetings yet held.

Delegates and the members of their families accompanying them were guests of the university and the colleges during the meeting. The cordial reception and delightful entertainment extended to them by their English colleagues will long be remembered by all who were privileged to attend.

The business sessions of the council and the general assembly were interspersed with scientific sessions at which papers on topics of general interest were presented. These papers had been printed in advance of the meeting and copies were placed in the hands of the delegates. Extended discussion followed the presentation of each paper and this feature of the program added greatly to the interest and value of the meetings. The following is the program of the scientific sessions: "The Nature of Soap Solutions," by J. W. McBain; "Recent Developments in Contact Catalysis," by E. K. Rideal; "New Aspects of Tautomerism," by J. F. Thorpe; and "Chemical Mechanisms Involved in the Oxidations Which Occur in Living Tissues," by F. Gowland Hopkins.

On Tuesday a special session of the Union was held, at which the Paterno Medal was conferred on F. W. Aston. On Wednesday at a special congregation of the university the degree of doctor of science, *honoris causa*, was conferred upon the following delegates: Wilder Dwight Bancroft, professor of chemistry in Cornell University; Ernst Julius Cohen, professor of chemistry in the University of Utrecht; Albin Haller, president of the Academy of Sciences of the Institute of France; Charles Moureu, professor of chemistry in the Collège de France; Raffaelo Nasini, professor of chemistry in the University of Pisa; Amé Pictet, professor of chemistry in the University of Geneva; and Frédéric Swarts, professor of chemistry in the University of Ghent.

At the first meeting of the council the annual address, in which the work of the Union for the past year was reviewed, was given by the president.

The business sessions of the council and of the general assembly were occupied with the receipt and discussion of committee reports and resolutions. The full report of the business transacted and of the various actions taken by the Union will appear in the *Comptes rendus* of the meeting and a summary thereof will appear in a later issue of THIS JOURNAL as soon as the official reports are available from the office of the secretary.

The admission of Brazil as a member of the Union was unanimously approved by the council, the application for admission having come from the Brazilian government.

On invitation from the Danish delegates, the Union voted to hold its 1924 meeting in Copenhagen.

After the adjournment of the Union many of the delegates remained in Cambridge in order to attend the sessions of the Society of Chemical Industry, which held its annual meeting the latter part of the same week.

The American delegates at this meeting were as follows:

Members of the Council

W. D. BANCROFT, *Chairman*
E. W. WASHBURN, *Secretary*
G. N. LEWIS
R. E. SWAIN
W. A. NOYES
J. E. ZANETTI

Members of the General Assembly

HAROLD HIBBERT
PAUL E. HOWE
V. K. LA MER
A. P. MATHEWS
W. A. NOYES, JR.
M. S. SHERRILL
GRAHAM EDGAR
A. P. SAUNDERS
D. S. CHAMBERLIN

Calendar of Meetings

American Chemical Society—66th Meeting, Milwaukee, Wis., September 10 to 15, 1923.

American Association for the Advancement of Science—77th Meeting, Los Angeles, Calif., September 17 to 20, 1923.

Ninth National Exposition of Chemical Industries—Grand Central Palace, New York City, September 17 to 22, 1923.

American Electrochemical Society—Fall Meeting, Dayton, Ohio, September 27 to 29, 1923.

American Institute of Chemical Engineers—Winter Meeting, Washington, D. C., December 5 to 8, 1923.

NOTES AND CORRESPONDENCE

Witnesses in the Foundation Suit

Editor of Industrial and Engineering Chemistry:

It seems to the writer that there should be recorded a list of the witnesses who testified in the suit of the United States Government against the Chemical Foundation in the United States District Court at Wilmington, the hearing having been concluded July 23. It is interesting to note how different interests were aligned and with whom those concerned preferred to class themselves. The following were called by the Government:

Karl Holdermann, director of Badische Anilin und Sodafabrik
Albert M. Patterson, a prominent industrialist and president of the Textile Alliance, Inc.
Harry E. Danner, treasurer of the American Dyes Institute
Will T. Gordon, formerly an attorney in the Bureau of Investigation, Alien Property Custodian's office
Frank L. Polk, Undersecretary of State 1918–19
Harry S. Brown, of the Alien Property Custodian's office
W. H. Swenarton, a patent attorney at one time in the Nitrate Division, Army Ordnance
G. W. Storck, a certified public accountant of the Department of Justice
C. R. Parmele, president of the Chinosol Company, manufacturing chemists
Mrs. Margaret R. Wilson, of the Federal Trade Commission
Harry W. Schmits, an accountant in the Alien Property Custodian's office
Herman A. Metz, president of H. A. Metz & Company, and connected with other industrial concerns
Thomas W. Miller, Alien Property Custodian since March 12, 1921

These witnesses were called by the Government in rebuttal:

H. J. Galloway, special assistant to the Attorney General
Geo. W. McCoy, director of the Hygienic Laboratory
Walter G. Christiansen, research chemist at the Harvard Medical School
Louis Freedman, research chemist with H. A. Metz & Company
William O. Emery, Bureau of Chemistry
H. D. Gibbs, formerly with the du Pont Company and now with the Hygienic Laboratory
Paul A. Blair, a patent attorney of the Bureau of Ordnance, Navy Department
Chester N. Myers, chemist with H. A. Metz & Company

The witness appointed by the court to supervise the experiment of Dr. Freedman was Gellert Alleman, professor of chemistry at Swarthmore.

It should be noted that several of the witnesses called by the Government, including Messrs. Polk, Patterson, Danner, and McCoy, proved disappointing as witnesses for the prosecution, their testimony being favorable to the cause of the Chemical Foundation.

The witnesses for the Foundation were as follows:

A. Mitchell Palmer, formerly Alien Property Custodian
Francis P. Garvan, president of the Chemical Foundation, Inc.
Joseph H. Choate, Jr., attorney
Ernest H. Volwiler, of the Abbott Laboratories
B. W. Dold, public accountant
Henry B. Thompson, president of the U. S. Finishing Company
Franklin W. Hobbs, president of the Arlington Mills
Frank D. Cheney, president of Cheney Brothers
Andrew W. Imbrie, treasurer of the U. S. Finishing Company
Julius Stieglitz, University of Chicago
William W. Buffum, auditor, Chemical Foundation, and formerly chief accountant, Alien Property Custodian's office
Charles L. Parsons, consulting chemist
Alfred H. White, professor of chemical engineering, University of Michigan, formerly lieutenant-colonel in the Nitrate Division, Army Ordnance
Harry A. Curtis, director, Nitrogen Survey for the Department of Commerce, and professor of chemical engineering, Yale University
James F. Stiles, Jr., accountant of Abbott Laboratories
Elmer K. Bolton, director of the Chemical Section of the Dyestuffs Department, du Pont Company
Ernest H. Klipstein, president, E. C. Klipstein & Sons Company
T. W. Still, treasurer, E. C. Klipstein & Sons Company
M. L. Crossley, chief chemist, Calco Chemical Company
James B. Eliason, comptroller, du Pont Company
M. R. Poucher, director of du Pont Company, and previous to 1915 vice president of Badische Company of New York

At the counsel table for the Government was to be found H. W. Anderson, special attorney in charge of the prosecution, and among his assistants were H. J. Galloway, District Attorney Hughes, Special Patent Counsel Knight, and during the last few days of the trial H. D. Gibbs as chemical adviser.

The trial counsel for the Foundation was Isidore J. Kresel, and counsel attending were W. D. Guthrie, L. H. Boggs, Bernard Hershkopf, and S. M. Stellwagen.

It will probably be many a day before a trial of equal interest to so many chemists and chemical industries engages the attention of our courts, and the individuals who are prominent in it are here recorded for the benefit of those who did not find it possible to follow the developments as they unfolded day by day.

103 Park Ave.
New York, N. Y.
August 15, 1923

J. Merritt Mathews

Viscosities of Sulfuric Acid-Water Mixtures

Editor of Industrial and Engineering Chemistry:

In This Journal, **15,** 850 (1923), Rhodes and Barbour state that their values for the viscosities of sulfuric acid-water mixtures are much lower than those of Dunstan and Wilson [*J. Chem. Soc. (London)*, **91,** 85T (1907)]. In the case of an 84.5 per cent acid, Rhodes and Barbour found a viscosity of 20 centipoises, while Dunstan and Wilson found a viscosity of 94 centipoises.

In an investigation of the fluidities of ternary and binary mixtures of nitric acid, sulfuric acid, and water conducted by Dr. Bingham and myself, the same difficulty was encountered. We were fortunate enough to discover a later article by Dunstan [(*Proc. Chem. Soc.*, **30,** 104 (1914)] in which he states that a constant numerical error was present in all his values for sulfuric acid-water mixtures. The values given should therefore be multiplied by 0.2325. Applying this factor to the case of the 84.5 per cent acid, Dunstan and Wilson's value is reduced to 21.8 centipoises, and is brought in much better agreement with the value of Rhodes and Barbour.

Bradford Stone

Lafayette College
Easton, Pa.
August 7, 1923

Atmospheric Pollution by Industrial Wastes

In the paper, published in This Journal, **15,** 296 (1923), the second sentence in the fifth paragraph on page 298 should read: "A plant will endure nearly eight times the concentration of sulfur dioxide at 10 per cent relative humidity that it will in a humid or moist atmosphere."

Robert E. Swain

WASHINGTON NOTES

Treasury Department Promulgates Dye Standards

The long-awaited standards of strength for assessing customs duties on coal-tar products imported under Paragraph 28 of the Tariff Act of 1922 have been promulgated. Tentative standards were announced last May, but the final drafting of the regulations was delayed pending consideration of criticisms and suggestions received and a report from the customs authorities. The official list contains an initial key index, indicating the name of the manufacturer of each dye. Selection of a dye as of standard strength does not guarantee its quality, but merely indicates that the dye has been selected as of fixed strength for the purpose of assessing duties.

Adjust Your Carburetors and Save Gasoline

Experiments made by the Bureau of Mines on the fleet of motor trucks used by the Government Fuel Yard indicate that substantial savings may be made in gasoline by the periodical adjustment of carburetors based on the results of analysis of exhaust gases from automobile engines. As the result of carburetor adjustments made by gas analysis, an actual increased efficiency in mileage and saving of gasoline amounting to 22 per cent was attained. The tests demonstrate that a portable carbon dioxide indicator for testing the exhaust gases of a motor vehicle gives a positive indication of the carburetor adjustment, removes all guess work of such adjustment, is perfectly feasible, and is almost indispensable to a company having ten or more large trucks in service.

Industrial Alcohol Regulation

A joint committee, representing the Alcohol Trades Advisory Committee and the Prohibition Unit, has completed the revision of regulations No. 60, under which intoxicating liquors are manufactured, distributed, and used.

Among the most important changes in the proposed regulations which have been tentatively agreed upon, is one which will provide that permits for certain classes of operations when once granted may continue in effect until revoked or suspended for cause or surrendered by the permittee. Permits to manufacture, sell, or transport will continue as at present to require annual renewal if they are to remain operative, but after the new regulations go into effect the basic permits for other classes of operations will not require such annual renewal. It is expected also that the new regulations will define more clearly than the present regulations the conditions under which permit privileges may be temporarily suspended or permanently revoked by the Prohibition Commissioner.

Among other important changes tentatively agreed upon may be mentioned those fixing the standards for flavoring extracts and other preparations; stating more clearly and specifically the requirements as to records and reports to the office by persons operating under permit; and making more definite and specific the provisions of the regulations which fix the quantity of liquors which may be used or dealt in by permittees.

Platinum Swindle

The Bureau of Mines warns the public to scrutinize carefully offers of stock in so-called platinum-producing companies proffered by unscrupulous promoters. Although the United States, from widely scattered sources, produces only a few hundred ounces of platinum a year, certain promoters have made extremely fanciful announcements regarding properties claimed to contain platinum in commercial quantities. These promoters bolster their claims by the display of erroneous assays, which, in some instances, have reported values as high as $25,000 worth of platinum to the ton. In one instance, the assertion was made that a property near Yonkers, N. Y., contained 10,000,000 tons of rock bearing this precious metal, the values ranging from $200 to $600 per ton—a mere bagatelle of from two to four billion dollars! In the case of a Seattle, Wash., concern, the possession of ore containing platinum and gold "in astonishing quantities" was heralded, while the location of the deposit was kept secret, in order to forestall a "mad rush." Numerous samples of alleged platinum-bearing ores from various properties examined by assayers of the Bureau of Mines at Reno, Nev., have failed to disclose the presence of platinum in appreciable quantities. In some instances, definite evidence has been obtained of the "salting" of samples with platinum wire and foil.

The growing seriousness of the situation created by unscrupulous promoters of alleged platinum-producing properties has suggested to various state mining officials in the western states the necessity of taking some action to protect the public. Legal prosecution has been considered but not hitherto employed, owing to the lack of sufficient laws to reach the cases, also to the difficulty of securing evidence of the necessary character. Legislative relief has been considered in the form of a law requiring the licensing and examination of assayers, and the so-called "blue sky" laws have also been considered as a possible remedy. Little or no progress has been made toward the eradication of the evil.

The Bureau of Mines advises persons who are asked to speculate in a platinum property to let it alone unless the purchaser is prepared to go to the expense of a careful examination by a competent engineer.

Tariff Commission Activities

C. R. DeLong, who sailed for Europe on May 3, returned to the United States on August 21 and brought with him production costs as a result of the investigations which he conducted on the following chemicals in the places named: barium dioxide, linseed oil, cresylic acid, and phenol in England; barium dioxide in Germany; diethyl barbituric acid in Switzerland; linseed oil and oxalic acid in Holland; and barium dioxide in France. He was unable to obtain production costs on sodium nitrite in Norway and Germany and on potassium chlorate in Germany, but valuable general information was procured. These figures will be tabulated and reports prepared, as a result of which it is probable that hearings will be announced shortly.

The Tariff Commission has ordered investigations under the flexible provisions of the tariff of the rare sugars, amino acid and amino salts, not of coal-tar origin, and of magnesite and magnesite brick, and has set October 1 to hear petitions for reduction in the duties on magnesite. Under its general powers, irrespective of the Tariff Act, the Commission has announced that a general survey will be made of thymol, including thymol crystals. It has just issued a resumé of its findings on casein, which gives the average costs of production in this country and Argentine, exclusive of the skimmed milk costs.

The commission has postponed until September a decision on the application for a reduction in the duty on soy bean, coconut, peanut, and various fish oils.

C. H. Penning has gone to Haiti and Jamaica in connection with the logwood extract investigation.

W. G. Campbell to Be Director of Regulatory Work

Walter G. Campbell, at present acting chief of the Bureau of Chemistry, has been appointed Director of Regulatory Work of the Department of Agriculture, a new position created by Congress. Mr. Campbell will assist the Secretary of Agriculture in administering the law enforcement work of the department. He will assume his new duties about October 1. Among the regulatory acts of which Mr. Campbell will have general supervisory administration are the Food and Drugs Act, the Insecticide and Fungicide Act, and the Naval Stores Act.

Leather Specifications

The leather section of the Bureau of Standards has completed a final draft of specifications covering rawhide for vegetable-tanned sole leather. These specifications were prepared for presentation to the subcommittee on leather of the Federal Specifications Board. The approval of the Tanners' Councils committee has been secured, and an initial draft of specifications for three grades of upholstery leather has also been prepared. The data upon which these specifications are based have been prepared from an investigation which has just been completed upon upholstery leather samples submitted by automobile manufacturers.

Tires from Reclaimed Rubber

The Bureau of Standards has placed an order with a rubber company for the making of fifty tires, using various amounts of reclaimed rubber in the treads. After manufacture, these tires are to be tested in the laboratory and also on trucks of the Post Office Department over four different types of roads, so that the relative wear of the different compounds can be determined.

August 23, 1923

CANADIAN LETTER

By S. J. Cook, 140 Broadway Ave., Ottawa, Canada

INSULIN

The most outstanding event of the year in the field of medical and biochemical research has been the development of the production of insulin at Toronto University and its application in the treatment of diabetes the world over. Much progress is being made in the Connaught Antitoxin Laboratories at Toronto, where the entire Canadian supply is being produced under the direction of C. H. Best, collaborator with Dr. Banting, to whom the discovery is due. The patents for Great Britain are being handled by the British Medical Research Council; leading experts on the continent of Europe and in Japan have been given full information as to the process, and large firms are being licensed in the United States. So far the Eli Lilly Company of Indianapolis has been the coöperating firm and has put out an excellent product at low cost. Thus, the public has been protected from exploitation.

Honors have poured in on Dr. Banting, a modest, likable young man of an essentially retiring disposition. The governors of the University of Toronto have named him Professor of Research in Medicine. The Faculty of Medicine has awarded him the Julius Mickle Fellowship, worth $1200, which is given every year in recognition of the greatest discovery made in the medical field during the past ten years. Last year it was given to Dr. Harvey Cushing of Boston, the great brain surgeon, and the year previous to Dr. Pavlov, the Russian physiologist. The Dominion government has voted Dr. Banting an annuity of $7500. The Canadian National Exposition, held annually at Toronto, has invited Dr. Banting to open the great fair this year, and as a further mark of recognition has announced that this will be "Science Year" at the exhibition.

BRITISH EMPIRE EXHIBITION

Government departments and industrial organizations are coöperating in the preparation of what promises to be the finest exhibition of Canadian industrial and commercial progress ever produced and the assembled material will be housed in the mammoth Canadian building at the British Empire Exhibition to be held next summer at Wembley Park, near London, England. One-half of the ground floor space will be devoted to general displays portraying such activities as the movement of grain from western farms by rail to the elevators, thence by water to the eastern outlets to foreign markets; another will be illustrative of Canada's water powers, developed and undeveloped, while extensive panoramic scenes will deal with the progress of agriculture, mining, fishing, and the principal phases of manufacturing. The remaining half of the ground floor space will be filled with industrial booths, manned by Canadian manufacturers seeking empire trade. The Dominion government through its Department of Trade and Commerce is providing every facility for the arrangement and planning of these exhibits, and has set aside well over half a million dollars for the purpose of promoting and conducting Canada's participation in this empire exhibition. Thousands of people from all parts of the empire will visit the great show in London next year, and it is probable that many from the United States will also be there.

USES OF NONMETALLIC MINERALS

A special survey of the consumption of nonmetallic mineral products, particularly those used in a finely divided state, is now being carried out by the Dominion Bureau of Statistics at Ottawa. In recent years, considerable quantities of Canadian feldspar, particularly, have been exported, mostly to the United States, where it has been finely ground and then sold, some of this product being returned to Canada, but most of it being shipped to Europe. The development of a "substitute" market in nonmetallic minerals is considered quite possible. It is held that Canadian calcite can be ground finely enough and at a sufficiently low cost to permit of its use in preference to imported whiting. The substitution of ground mica for soapstone as a "slip" material between inner tubes and casings for motor vehicles has already been found practicable. Quantities of ground waste mica are also being sold to the manufacturers of composition roofing, who are said to find it preferable to sand in the preparation of some grades of roofing. The saving in this last item is in the quantity required.

DEVELOPMENT OF PETROLEUM INDUSTRY

Activity in the petroleum refining industry has been noticeable, particularly in western Canadian fields. A new refinery has been established at Lethbridge, Alberta, which for the present will treat crude oils imported from the company's wells in Montana. Another plant designed to work up Alberta products and to make road tars and asphalts more particularly is practically completed. The interest in the oil fields farther north continues and special parties are in the field with a view to locating new sources and to determine the commercial values of these fields.

Progress in the mineral industries of Alberta and of the manufacturing enterprises dependent on these minerals has been marked during the past two years, and evidence of the soundness of the provincial government policy of development through research by competent investigators is beginning to become apparent.

TARIFF CHANGES

The change in the Canadian tariff, whereby a bounty of 1.5 cents per pound is to be paid on copper bars and rods produced in Canada, has been received with general satisfaction. Although limited in time to the next five years, the assistance given copper rolling mills in Canada during that time will, it is considered, be sufficient to permit the establishment of these plants on a firm basis.

Apart from the item noted, the tariff changes this year were of little moment. The present minister of finance, The Right Honorable W. S. Fielding, having prepared and defended sixteen budgets prior to the one brought down by him this year, is not one to introduce startling innovations into the Canadian tariff, and interested as he has been for many years in the promotion of reciprocal trade agreements, especially with the United States, he requires that a plea for the protection of a new venture by tariff imposts be very firmly supported before being given even cursory attention. The promotion of Canadian trade is paramount; if this necessitates, at times, the imposition of tariff restrictions, such changes are only made after mature deliberation and a careful weighing of all the facts.

NICKEL AND COPPER

The revival in the nickel and copper industries during the past few months has been a matter of considerable satisfaction to the general public as well as to the firms actually engaged in the industry. The British America Nickel Corporation has been reorganized and Charles A. Rose has been appointed general manager in succession to E. J. Carlyle, who recently retired after many years of active work in which he made a name for himself by his efficient management and broad-gage ability to get results. Mr. Rose takes up a difficult task, as the plants have all been closed for more than a year and the staffs have been scattered. The markets for nickel and copper have been greatly depressed; conditions are quite different from those prevailing either during the war when demand was at the peak, or before the war when only smelting operations were carried on in Canada. Mr. Rose brings to his work seventeen years' experience in some of the largest United States plants, and those who know him predict a continuance of the success which has marked his work in the past.

The International Nickel Company and the British America Nickel Corporation both operate smelters and refineries in Canada. The Mond Nickel Company smelts its ore to a matte, which is then shipped to Swansea, Wales, for further treatment. The capital invested in Canadian nickel-copper smelters and refineries is reported to be about $37,000,000, so that the revival of operations and consequent earning power is naturally pleasing.

August 7, 1923

Edward Mallinckrodt of St. Louis has given $500,000 toward the construction of a group of new chemical laboratories for Harvard University. The building will bear the donor's name and will stand between the new lecture hall and the university museum, near the Wolcott Gibbs and Coolidge laboratories.

LONDON LETTER

By Hugh Griffiths, 15 New Bridge Street, London, E. C. 4., England

Chemists' Agreements

The legal obligations of a chemist in this country have often been the subject of discussion, but an authoritative statement from a competent source has not hitherto been readily available. The Institute of Chemistry has now, however, issued a booklet giving a complete account of a lecture by E. J. MacGillibray, barrister-at-law, on "Some Aspects of the Law of England Affecting Chemists."

It is usual in this country for an employer, after a probationary period, to engage a chemist under agreement for a period of three years or more, and to provide in the contract certain clauses restraining the chemist from afterwards entering the service of a competitive firm. Some of these agreements have been bitterly unjust to the employee, and chemists have generally been resigned to the belief that they must regard such agreements as inevitable in every large works. The legal value is doubtful, and it is now explained that some of these agreements cannot be enforced by legal process, except perhaps in flagrant cases where the chemist dishonestly transfers his services to a competitive firm with the intention of disclosing manufacturing secrets which were exclusively the property of his original employers.

The Dyestuff Situation

The Key Industries Act is again claiming some attention, and at present a very solemn and serious discussion is in progress on the question as to whether formaldehyde is a synthetic chemical. The usual hair-splitting arguments have been heard, and presumably very soon the referee will throw out a decision. A most serious feature arising in the discussion is that certain firms, relying upon the circumstance that formaldehyde was a scheduled product, have erected plants for the manufacture on a large scale, and the attempt to take away from them the small measure of protection given by the act places these firms in a difficult position.

In spite of the general uncertainty regarding restrictions on importation, the dyestuff situation has developed very considerably. The British Dyestuffs Corporation has been able to report an increase of profit in spite of the reduction in prices during the year. After providing £411,000 for depreciation and crediting the sum to be recovered in respect of excess profits duty, the year's profit balance amounts to nearly £103,000. The situation is, however, not without great difficulties, but in view of the circumstance that enormous sums of money have had to be spent in research and there has been a conflict of interests between the dye manufacturer and the dye user, this year's work is most encouraging. A complicated and delicate machine such as the dyestuff industry would be difficult enough to establish even under normal trade conditions, and prodigies of organization are necessary, and the balance of trade interests must always be of great importance. In England, however, there is a Colour Users' Association, representing stronger and perhaps nationally much more important industries than the dye industry, and this association has been endeavoring to get an official pronouncement regarding the price of dyestuffs. This association has suggested that import licenses for any dyestuff should be given in the event of the home price being higher than the foreign price, or more than three times the pre-war price, whichever of these alternatives happens to be the greater. The dye manufacturing interests do not feel that they are able to accept this proposal, and they point out that such an offer would only be sufficient to cover the difference between the costs of production to-day and those prevailing before the war, and that there would be no margin which could be devoted to the systematic development of the industry, and while many of the products can be, and are, sold within the price basis mentioned, the universal application of such a rule would be disastrous to the industry. With this attitude most chemists will find themselves in agreement. The comparison of prices of British-made dyestuffs is interesting. A year ago the average price of colors sold by one company was 3s. 5d. per pound, the average price to-day is 2s. 6d. per pound.

At the annual general meeting of the Association of British Chemical Manufacturers recently held in London, this question was again discussed from the chair, and the agitation in certain quarters for the repeal of the Dyestuffs Act was again mentioned. It was suggested that perhaps the real trouble facing the textile industry was the high price of cotton and the difficulties in the far eastern markets. This association, which has been formed to protect the interests of the chemical industry, has devoted its attention to the excise restrictions on the use of alcohol in chemical manufacture, and has at last succeeded in obtaining a very reasonable and important concession. The chemical manufacturer may now use quantities of alcohol up to 100 gallons without special storage equipment, and without the attendance of the excise officers, the only obligation being that a proper record of the destination of the alcohol has to be kept. This alcohol question has always been a very serious one to the fine chemical manufacturer in this country, and although it has been possible to obtain slight concessions from time to time under special circumstances, the trouble and routine necessary has made manufacturers inclined to give up the manufacture of materials requiring alcohol rather than face the difficult conditions imposed by excise regulations.

Viscous Flow and Heat Transmission

Some time ago the writer read a most interesting paper by D. Wesson, entitled "Some Wild Engineering I Have Known," or words to that effect. In this paper a number of chemical engineering blunders are mentioned, one of them referring to the dimensions of a pipe for carrying a stated volume of liquid with a certain available pressure difference.

In spite of the wildness of the result mentioned in this paper, it must have occurred to many readers that the design of a pipe line in a chemical works is not a very easy matter. It has hitherto been the practice to calculate the pipe sizes by the ordinary formulas used for water, afterwards making some sort of intelligent guess as to what the result would be for oil, glycerol, vitriol, or whatever fluid had to be handled. Such a procedure was of course not without dangers, and "horse sense" had to be relied upon to provide ample dimensions. A totally different method of calculation for design is that based upon the researches of Stanton, who with his collaborators has investigated problems of pipe friction, and has arrived at a scientific criterion on which the similitude in conditions may be calculated. This method has already been dealt with in a considerable number of scientific papers and in at least one book devoted to chemical engineering work. It is safe to say that with this method which when once mastered is not too elaborate for practical work, the number of examples of "wild engineering" would be diminished.

The conditions existing in a fluid passing through a pipe are no doubt complex, and the dynamical problems presented have to be solved by methods of similitude calculation, rather than by orthodox mathematical processes. It is obvious that if the dynamical problems partake of this nature, the thermal problems, particularly those relating to heat transmission, must of necessity be similar.

The first real scientific contribution to the subject of heat transmission is probably that found in the work of Osborne Reynolds, who at least stated the problem fairly accurately, and did not merely attempt to derive coefficients, which have to be altered often by several hundred per cent to compensate a slight variation in conditions. Most of us who have had to do with the design of chemical plants depending upon heat transmission problems will know that, although thousands of researches have been published very little information can be collected for practical purposes of design, except in so far as the coefficients derived relate strictly to a typical design of apparatus operating under fairly well-known and well-established conditions.

The British government published recently a volume of the "Technical Records of Explosives Supply" entitled "Heat Transmission." In this volume a somewhat more scientific method of attack is presented, but the treatment is, although an advance, not very remarkable.

Some papers are at present appearing in the weekly *Engineering*, entitled "The Laws of Heat Transfer," in which the subject is being attacked differently, and the criterion of fluid friction is employed in an endeavor to calculate the "film resistances" to heat transmission. These articles, which are of greatest interest to the chemical engineer, are anonymous.

July 20, 1923

BOOK REVIEWS

Wood Distillation. By L. F. HAWLEY. American Chemical Society Monograph Series. 146 pp., tables, diagrams, and illustrations. The Chemical Catalog Co., Inc., New York, 1923. Price, $3.00.

This work is in reality two monographs, Part I being concerned with hardwood distillation and Part II with resinous wood distillation. As the author states in his introduction, there is absolutely no connection between the two industries nor are there any but apparent resemblances between the processes and methods employed.

The author's purpose, as stated in the introduction, is to present for each subject a brief outline description of present chemical practices for each of the two separate parts, as a basis for the discussion, as he says, of the chemistry of the raw materials, the processes, and the products. While this plan has been followed, the treatment is so broad as to have warranted the title "A Discussion of the Physical and Chemical Principals Employed in Wood Distilling Industries and the Direction in Which Improvement Must Be Sought." Again quoting from the introduction, "this work is the result of the author's long connection with the Forest Service which has made possible frequent inspection of commercial plants and a large amount of research" on the specific subjects treated. The work will be of absorbing interest to all who are engaged in, or conversant with, the present state of this industry, which is undergoing a scientific resurrection from a long period of doldrums.

The work is saturated with information in the form of concise tabulations of observed facts, further illustrated by charts, graphs, and pictures. By these means Dr. Hawley has contrived to reduce to 146 pages about all the useful information that has survived the careful research and investigation of many years for both industries.

While many of the subjects handled lead to discussions of a highly technical character, the style is easy and interesting to follow and the conclusions leave the reader well paid. Many of the engineering features of plant and process are purposely omitted, such, for example, as the direction by which improvement could be expected in the design and operation of retorts, and the author purposely omits any discussion of acetic acid, formaldehyde, or acetone, and only makes brief reference to the refining of wood alcohol, turpentine, and pine oils. Evidently, his purpose is to confine this work to subjects that will afford the most help to the wood distiller as distinguished from those concerned with the derived products. In some cases he bluntly states that the discussion is omitted because he does not know the answer, or, as he says, "from a disinclination to copy from the literature without that first-hand information which gives the necessary skill in selection and criticism." The author's modesty is in some respects a handicap, as he is known to possess a vast store of information on several of these excluded subjects which would be of great general benefit, though as yet incomplete from his own more exacting point of view.

Many pictures serve to keep the reader in touch with familiar aspects of the industry and thus allay apprehensions of the timid while they are being led through discussions of subjects that might otherwise appear formidable. It is unsafe to skip any of these discussions because the practical application of the treatment is too valuable to lose.

An important feature of the work, perhaps the most valuable, is the criticism and corrections of information and data current in the literature, some of which has passed unchallenged for fifty years. Conclusions based on investigation in Europe have long been accepted as basic, which under the author's careful research have been found to be subject to important modification and in some places are completely refuted.

The tabulated results of experimental distillations of American woods, both hard and resinous, would alone make the book priceless to wood distillers who seek improved yields and quality of products.

WALTER E. LUMMUS

A Tested Method of Laboratory Organization. By SEYMOUR PILE AND REGINALD JOHNSTON. 98 pp. H. F. & G. Witherby, London, 1923. Price, 7s. 6d. net.

In 1917 a number of Birmingham manufacturers of brass and copper alloys united to form an organization which they called the "Midland Laboratory Guild, Limited," to make a serious attempt at coöperation in the scientific control of industry and in the establishment of a coöperative chemical and physical laboratory.

A building was obtained, and each of the member firms paid a sum as entrance fee which in the aggregate was sufficient to equip the building as a chemical and physical laboratory.

Events have proved that this coöperative laboratory has not only been successful in stimulating the technical progress of the firms involved, but has provided a common meeting place for the mutual discussion of problems, and such a coöperative laboratory is valuable as illustrating how in small industries and among small manufacturers the financial problem can be solved.

There is a valuable preface to the book contributed by W. R. Barclay, from which much of this review is drawn. On the general subject of works laboratory organization there is room for much discussion, and many differences of opinion exist among technical men as to the scope of a works laboratory and its relationship to the works itself. Some things said by the authors of this book will undoubtedly provoke criticism, but, at least, it may be said that they have performed a valuable service to industrial organization in general by putting forward their views.

The authors do not appear to be aware of any other books on the subject of laboratory organization, and, indeed, state specifically in their preface that so far the scientific laboratory seems to have escaped attention from the authors of books.

The design of the laboratory building and the method of taking samples and recording analyses are discussed at considerable length, and these chapters will undoubtedly be of value to any one planning a laboratory for similar work. There is also much general discussion of the personnel of the laboratory and of the internal relation of the members to each other. A special system of costing was necessitated by the coöperative nature of the work, and would seem to be suitable for the special circumstances of this laboratory.

The book does not give full consideration to the subject of research laboratories, the laboratory described apparently having devoted almost all its attention to testing and analysis, research being referred to as merely incidental to these other activities. Fundamental work is almost ignored. The chief value of the book lies in its careful and detailed account of the experience which the authors have had. Its chief defect is the absence of any general knowledge of what has been done in industrial laboratories of other types.

C. E. K. MEES

Chemisch-Technische Vorschriften. Ein Handbuch der speziellen chemischen Technologie insbesondere für chemische Fabriken und verwandte technische Betriebe enthaltend Vorschriften aus allen Gebieten der chemischen Technologie mit umfassenden Literaturnachweisen. Band I—Metalle und Minerale. By OTTO LANGE. 1011 pp. Otto Spamer, Leipzig, 1923. Price, paper, $8.00; cloth, $9.00.

This work, encyclopedic in character, is really a handbook of methods for the chemist and chemical engineer. It aims to answer the questions: How does one prepare or manipulate a certain product; and what are the intermediate or final products? It also furnishes literature or patent references to practically every statement made. Nearly all the references are to German sources, citations from German abstract journals replacing references to the original source. Because of the nature of the work, no critical discussion of the statements contained therein is attempted.

The work is to consist of four volumes: I—Metals and Minerals; II—Fibers, Leather, Bones, Celluloid, Artificial Plastics, etc.; III—Resins, Oils and Fats, Rubber, Petroleum, Soaps, etc.; IV—Fertilizers, Explosives, Foods, and Feeding Stuffs.

Volume I discusses the metals, natural and artificial silicates, ceramics, glass, alkali and akaline earth metals and compounds, mortar and cement, artificial stone and mineral colors. The method of treatment and scope of the work is seen from the following list of topics under the heading "Iron" (100 pages): occurrence, properties and uses, preparation, alloys, corrosion of iron and means of preventing corrosion, galvanizing, sherardizing other metallic coatings, nonmetallic rust-preventing agents, enameling of iron.

The volume is provided with a 38-page index which appears to be very complete. C. J. WEST

Taschenbuch für die Farben- und Lackindustrie. By HANS WOLFF and W. SCHLICK. 4 × 6¼ inches. Wissenschaftliche Verlagsgesellschaft m.b.H., Stuttgart, 1923.

This little book is divided into two distinct, separately bound parts, which are fitted into a single cover. The "Farben-und-Lackkalender," containing 177 pages devoted to analytical and descriptive data and a few manufacturing formulas of interest to the paint and varnish chemist, is permanently bound to the cover. The "Schreib-Kalender" consists of the usual diary with about fifty pages of advertising matter, and is arranged to fit into the cover in such a way that it may be replaced with a later edition for next year.

In the first part there is nothing of a technical nature that is particularly new or striking. The authors state their purpose to be the preparation of a practical book for the practical man, and hence are to be excused from the inclusion of new and untried material. It is quite probable, too, that they have encountered the characteristic reticence of manufacturers to let their latest developments be published. Among their manufacturing formulas there is scarcely one which cannot be found in as good, if not better, form in the notebook of every practical varnish or paint maker.

Probably the most interesting and at the same time the most practical part of the book is devoted to minutiae of plant practice which few books contain. Reduction of fire risks, trade-union rules (made necessary by the variety of rules being promulgated in Germany from time to time by the labor unions), and a chapter on the various trade usages in connection with the paint and varnish materials, are quite useful and novel in such a work.

The entire get-up of the book is cheap. The paper and printing are of very low quality, and the proof-reading has not been carefully done. One of the tables included, for instance, deals with equivalents of various foreign measures. Here we find this remarkable statement, "United States of America, One Bushel = 8 Quarts."

By-product Coking. By G. STANLEY COOPER. 2nd edition, revised by ERNEST M. MYERS. 192 pp. Benn Bros. Ltd., London, 1923. Price, 12s. 6d.

The first edition of this work appeared in 1917. While some new material has been added to bring the work more up to date, the new book is for the most part merely a reprint of the first edition. The greatest change is the addition of a new chapter on condensers and scrubbers. Other minor changes of no great importance have been made throughout the book.

The purpose of the book is best expressed in the words of Mr. Cooper: "In the text it has been the endeavour of the writer to steer clear of intricate technical explanations, and also to avoid chemical formulae, etc., which would not be intelligible to the average reader. The book is intended primarily for the student, but it is hoped that it may be found useful in a degree to the experienced man *****." The book should fulfil its purpose, for a comprehensive but abbreviated outline of the subject is given, although its usefulness to the experienced man is problematic.

One phase of the subject has not been dealt with—namely, that of gas purification. Undoubtedly, this is not a universal practice at coke plants, but it would seem that some mention should have been made of the subject. Perhaps it was the desire of the author for brevity that occasioned this omission.

The reader should bear in mind that the typical plants and processes are largely taken from English practice. In a more extended treatise one might wish for a clearer description of American practice, but it is hardly fair to expect a more complete treatment in a book of this scope. This work should be welcomed by students and any others who are desirous of obtaining a short and nontechnical description of the by-product coke-oven industry. A. A. KOHR

Tested Methods of Non-Ferrous Metallurgical Analysis. By SEYMOUR PILE AND REGINALD JOHNSTON. 127 pages, 10 figures. 5 × 7¼ inches. H. F. & G. Witherby, London, 1922. Price, 7s. 6d.

The authors present individual "Assays in Alphabetical Order of Metals" for twenty-three elements. Some cross references are made, but these are entirely too few. For example, the simultaneous electrolytic determination of copper and lead is not mentioned, nor is the determination of iron and aluminium or of antimony and tin in the same sample considered. The methods are no improvement over those which are well known and in common use. It is surprising that the authors have found the determination of aluminium as aluminium phosphate to be "very satisfactory for pure aluminium metals," and that in the analysis of spelter they obtained 99.94 per cent of zinc by electrolysis of a zinc nitrate-sodium hydroxide solution with amalgamated copper gauze cathodes, as against 99.932 per cent by difference. Some obvious faults are: Desiccants are used indiscriminately in the carbon method; no reference is made to a hydrofluoric acid treatment of silica; the interference of iron in the separation of tin as metastannic acid is not mentioned; digestion with nitric acid is recommended for the separation of small amounts of antimony; a one-half hour settling period is specified in the bismuthate method; the method for cadmium is not accurate because cadmium sulfide is not the compound which is obtained by precipitation with hydrogen sulfide in acid solution.

The illustrations seem crude when compared with the usual idealized "set-ups," but are undoubtedly more true to laboratory life. In spite of the authors' warning that "the technical slang of the laboratory has been used," such expressions as "magneted," "wangles," "a good fielder," "insert the bung," and "policemaned" are somewhat startling, while "dissolved in the least convenient quantity of sulfuric acid" and "bulk allowed to evaporate" seem like carrying technical license too far. In the "Obiter Dicta" it is interesting to note "Never trust anybody's sampling but your own," "Never attach any value to the manufacturer's description of the composition of the alloy," and "Don't forget to subtract the weight of your filter ash."

The reviewer believes that the book is not well suited for student use, that it has a limited value as a reference text, and that its chief interest lies in showing what methods the other analyst is using.

G. E. F. Lundell

American Petroleum Refining. By H. S. Bell. 456 pp., 263 illustrations. D. Van Nostrand Co., New York. Price, $5.00.

The object of this book is to present, to those interested in petroleum refining, the fundamental information and data involved in the manufacture of petroleum products. The chemical properties are described in one chapter of 37 pages, the discussion really being confined to an outline of the elementary chemistry of the hydrocarbons. This description, together with that on physical characteristics, could be expanded to include more details and additional matter, which will naturally be missed by one using the book. The American Petroleum Institute modulus, showing the relation between petroleum hydrometer (A .P. I. degrees) readings and the corresponding specific gravity, was adopted about two years ago by the oil industry, through agreement with the U. S. Bureau of Standards. Consequently, Baumé degrees, used throughout the book, may be misleading. The outlines of methods for determining physical properties would be improved by the substitution of the adopted methods of the American Society for Testing Materials.

The descriptions of the manufacturing process and of the various apparatus are very good; much valuable data of a practical nature, including types of furnaces, stills, towers, condensers, and heat exchangers, about which center the real efficiencies of a petroleum refinery, are included. The theoretical considerations sufficiently illustrate the reasons for dimensions and arrangements selected in typical installations. Additional chapters have reference to special departments, such as filtering, wax, and lubricating plants, packages, acid recovery, transportation, etc.

The efficient operation of a modern refinery is impossible without a well-equipped laboratory, and more importance should be given to the subject in future editions. It is dismissed in a few sentences following several pages devoted to sanitary conveniences and consequently is difficult to find.

On the whole, this book is a valuable contribution to our petroleum technology, and one which should be in the hands of every one interested in petroleum refining.

C. K. Francis

The Spectroscope and Its Uses in General Analytical Chemistry. By T. Thorne Baker. 2nd edition. x + 208 pp. 98 figures. 5.5 × 8.5 inches. Wm. Wood & Co., New York, 1923. Price, $3.00.

The author has given us a remarkably useful book, and one which is far beyond the expectations engendered by the title. He has by no means limited himself to applications of spectroscopy in general analytical chemistry, as that term is usually interpreted. While the descriptions of the spectroscopes of various types and their accessories, together with their applications, constitute the main purpose of the book, the fields touched are broad, including, for example, fluorescence, Balmer's series, and X-ray analysis. While sufficient theory is given, the emphasis is on the practical side of the subject.

The various types and makes of instruments are described in sufficient detail to enable one to make a wise choice for whatever work is to be done, and the adjustments and technic are described adequately. The book is up to date and numerous references of work done in 1922 are to be found.

The first two chapters give the theory of spectroscopy and good descriptions of different types of spectroscopes. Possibly a somewhat more complete discussion of the plane grating and echelon grating would have been advisable. Refraction and resolving power are discussed in the third chapter. In Chapters IV and V the principal subjects discussed are: the spectrum in inorganic chemical analysis; flame, spark, arc, and vacuum tube spectra; illuminants; fluorescence and phosphorescence; chemical and heat energy of the spectrum; distribution of energy; the photo-electric effect and the infra red spectrum. Chapter VI contains an excellent discussion of spectrophotography and methods, and Chapter VII takes up the preparation of special photographic plates and filters.

Absorption spectra, spectrophotometry, and fluorescence are discussed in Chapter VIII. Chapters IX and X contain discussions of the Balmer series, atomic relations, the Zeeman effect, X-ray spectra, and X-ray analysis. The appendix gives useful information concerning the preparation of safe lights for development, silvering of glass, blackening of metals, and cleaning of gratings.

The typography, reproductions, and binding are excellent, and but few errors have been noted.

J. H. Mathews

The Phase Rule and Its Applications. By Alexander Findlay, M.A., Ph.D., D.Sc. 5th edition. xvi + 298 pages. 158 figures, 5 inserted as plates. 22 × 14 cm. Longmans, Green & Co., New York, London, Toronto, Bombay, Calcutta, and Madras, 1923. Price, $3.50 net.

The first edition of this well-known book was published in 1903, and for twenty years "Findlay" has been without a rival as an elementary text on the phase rule and its applications. Frequent revisions have kept it abreast of the rapid development of the subject by the inclusion of new experimental material; in this fifth edition many sections have been revised, and some new material has been added. The section on phosphorus has been rewritten, bringing in the work of Smits and Bokhorst and of Bridgman; and the treatment of sulfur has been amplified by the inclusion of a section on the work of Alexander Smith and of Aten on the pseudo-binary character of sulfur. The section on the iron-carbon alloys has been entirely rewritten in the light of the work of Ruer on δ-ferrite; LeChatelier's data for the dissociation pressure of calcium carbonate have been superseded by those of Johnston; the data for the system water have been revised; and the section dealing with liquid crystals has been largely rewritten. Frequent references are made to Smits' theory of allotropy, and Beilby's views as to the presence of amorphous material in worked metals are apparently accepted. The "complete" equilibrium diagram of the system H_2O–Na_2SO_4, as determined by Wuite, is included, but since the term "complete" is used, a further discussion of systems in which the critical curve is intersected by the solubility curve, and especially the relations at and above the second critical end point, would be advisable. The inclusion of the work of Rankin and Wright on the system CaO–Al_2O_3–SiO_2 and of van't Hoff on the oceanic salt deposits are valuable additions, but this value would be greatly enhanced by a little more discussion of these complicated systems. In addition to those enumerated, many minor revisions have been made, and the literature references have been greatly amplified. Findlay's "The Phase Rule and Its Applications" can be unhesitatingly recommended as the best elementary treatise on the subject, with the new fifth edition a material improvement over its predecessors.

George W. Morey

Trade Association Activities. Published by the Department of Commerce. 368 pp. Superintendent of Documents, Washington, D. C., 1923. Price, 50 cents.

This is a recent publication by the Department of Commerce—one of its series on elimination of waste—which merits careful reading.

In the introduction the Secretary of Commerce quotes the definition of a trade association as defined by the American Trade Association Executives: "A trade association is an organization of producers or distributors of a commodity or service upon a mutual basis for the purpose of promoting the business of its branch of industry or commerce and improving its service to the public." In the publication, which has been compiled with the assistance of many specialists, the principal legitimate activities of trade associations are defined as trade relations, employee relations, public relations, government relations, cost accounting, credit and collection, transportation, insurance, legislative statistics, commercial research, simplification and standardization, and industrial research.

Interesting chapters upon these topics and subdivisions are included and are followed by other chapters upon those government activities which are of immediate interest to trade organizations, with special reference to the various bureaus of the Department of Commerce. Due emphasis is given to similar relations with other federal departments and scientific bureaus.

The appendixes alone make the publication valuable to most readers, treating as they do the history of trade associations in America, trade associations abroad, and including a trade bibliography and a directory of national and international associations. This directory will be widely used, for it contains, besides an alphabetical list, a classification by commodity or service and a classification by functions.

That trade associations have a definite place and play a really important part in our industrial life is made clear by this publication. There are sufficient activities to engage the full energy of such associations and to justify their existence without their engaging in some practices that have recently found disfavor.

Industries as well as individuals are recommended to secure a copy of this document, which is written in a concise and readable form.

Coal and Allied Subjects. Being Bulletins 1 to 10 of the Lancashire and Cheshire Coal Research Association, 1918 to 1921, inclusive. By F. S. SINNATT AND ASSOCIATES. $5^1/_2$ × 7 inches, cloth, 205 pp. H. F. & G. Witherby, London, 1923. Price, 15s. net.

As indicated by the title, this publication is a collection of bulletins on sampling, analysis, determination of calorific value, and certain special analytical tests and investigations on coal.

Bulletin I covers ten introductory lectures on organic chemistry, with special reference to coal. These are presumably intended for engineers, mining students, and others of limited training in chemistry. The tables of physical constants have the common fault of many texts in omitting reference to the original sources. A brief discussion of the constitution of coal as worked out by Thiessen, Wheeler, Stopes, and others would have added to the value of the bulletin.

Bulletins II, IV, VII, IX, and X, on the sampling, analysis, and calorific value testing of coal, are the most generally useful bulletins in the book. The author has described the best methods and shows familiarity with recent progress in coal analysis.

Bulletin III, on the influence of the addition of inert matter upon the volatile matter evolved when coal is heated, and Bulletin VIII, on the inorganic constituents of coal with special reference to Lancashire seams, are of some interest to the highly specialized student of the chemistry of coal, but of doubtful practical value.

Bulletin V, on coal dust and fusain, is of interest to the coal-mine operator. It is shown that fusain (mother of coal) tends to collect in mine dusts and washing sludge. It may be an important factor in dust explosions, and Sinnatt has shown that it detracts from the coking property of coal.

Although well prepared, and of undoubted importance in connection with highly specialized research on coal, it is doubtful if the book, as a whole, is worth the price of 15 shillings to the American coal technologist.

A. C. FIELDNER

Fire Losses—Locomotive Sparks. By L. W. WALLACE. 1st edition. xi + 203 pp. 6 × 9 inches, illustrated. Barr-Erhardt Press, Inc., New York, 1923. Price, $3.00.

As stated in the preface:

> The purpose of this treatise is to set forth the facts disclosed as a result of some five years of intense investigation of locomotive sparks and their relation to fires occurring along the right of way of American railways.
>
> In conducting the investigations, every known question that had arisen in connection with law suits for damages from fires alleged to have been started by locomotive sparks was studied.

The book is divided into two parts and deals with fundamentals of locomotive construction, maintenance, and operation from the standpoint of the locomotive spark; the extent and seriousness of the fire hazard from locomotive sparks; the formation of the spark and means adopted to prevent its escape from the locomotive stack; the effect of various types and conditions of coal; the quantity and size of sparks ejected by different types of locomotives operated under various conditions of tonnage, speed, weather conditions, etc.; the weight and character of sparks caught at known distances from the center of the track; temperature at which a wide range in size and character will ignite dry combustibles; effect of wind velocity upon the height and distance to which sparks are carried; and the effect of different types of netting upon the quantity, size, and fire-carrying properties of locomotive sparks.

Important data not previously available are included and certain fundamental factors which have hitherto received too scant attention are stressed. The volume is gotten out in a most attractive form, is fully illustrated, bound in flexible leather, and should prove a valuable addition, not only to the library of the railway mechanical engineer, but to others working in applied fields.

White Lightening. By EDWIN HERBERT LEWIS. Covici McGee Co., Chicago, 1923. Price, $2.00.

This is a novel, not a treatise on chemistry or electricity. The reason for this notice is that here is a piece of literature written by a man who draws his illustrations as easily and more freely from chemistry than from the classics, and who evidently has more respect for the heroes of science than for those of mythology. It deals with the war, Indian lore, big business, out of doors, and sociological problems. In fact, it contains all the elements of modern fiction except the post-marital triangle, so skilfully interwoven in the romance that no one of them could be left out without a distinct loss to the continuity.

Some of the supposedly original achievements of the youthful hero may seem marvelous to those of us who know with what travail such ideas are brought forth, but perhaps such intellectual *tours de force* should be considered no more improbable than the physical accomplishments which we swallow without hesitation in most works of fiction. As is usually the case when a writer without exhaustive technical training deals with scientific matters, some statements are made which an expert might question; however, such slips are not frequent enough to seriously annoy the chemist or mislead the general reader. The book is clean, though distinctly not asexual. The English is modern and good, the style is clear, and the book is easy reading. The reviewer recommends this book to any of his confrères who enjoy fiction, and also to the public at large, which should get from its perusal a clearer idea of the proper position of science in the perspective of modern life.

WARREN RUFUS SMITH

COMMERCE REPORTS

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), poyable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

July

A development of considerable interest to American petroleum exporters is the recent announcement by the Argentine government of a project for the building of a complete **oil refinery** at La Plata, and a smaller refinery at Plaza Huincul, Argentina. (P. 17)

The Compagnie Occidentale des Produits du Petrole, of Paris, has under consideration plans for enlarging its facilities at Donges, which will make this plant the largest **petroleum** importing and distributing center in France. (P. 18)

A new method of making **coal gas** has been invented by C. B. Tully, an engineer of Newark-on-Trent, Nottinghamshire. Experimental work has passed the research stage. Mr. Tully has succeeded in reducing the amount of carbon monoxide in household gas below the usual 12 per cent. (P. 19)

The Italian Ministry of Industry and Commerce has appointed a technical commission to study the necessity for establishing standard specifications covering **petroleum products,** including gasoline, kerosene, lubricating oils and greases, fuel oils, etc. (P. 19)

A survey of **divi-divi** sources, development, and trade is described. The efficacy of this product as a tanning agent is exemplified in the significant increases in our imports since 1915, when it was generally adopted by American tanners. Its tannin content ranges from 40 to 45 per cent. (Pp. 32–33)

The scale of prices for the 1923–24 **nitrate** year, adopted by unanimous consent at the general meeting of the board of directors of the Italian Nitrate Producers' Association, is given together with corresponding prices for the year 1922–23. (P. 39)

Chemical fertilizers are being used more generously in Italy than at any time since the war. In 1922 one firm supplied 541,414 metric tons of superphosphates, as compared with 501,976 metric tons in 1921, and the strong demand for the spring of 1923 indicates that sales for the present year will reach 600,000 metric tons. (P. 39)

Two sources of natural **potassium nitrate** in the Caucasus are described. Both deposits are in the south Caucasus mountain range, approximately 40 miles to the southeast of Tiglis. One is located 6 miles south of the Dzegan railroad station. The salts contained therein have been proved by surface pits to be 80 feet deep. Analysis shows 3 per cent potassium nitrate. The second deposit, 15 miles from the Akstafa station, contains a large deposit which assays up to 10 per cent. (P. 39)

The preliminary figures for May, 1923, show that the United States **export trade in chemicals** has been rather spotty and irregular, with comparatively large shipments of a commodity in one month followed by small shipments in the next month. Nevertheless, the steady gain in the total exports of chemicals and allied products continued during the first months of 1923, until the aggregate value of May reached $13,365,572—the peak month for the year thus far, and an increase of 14 per cent over May, 1922. Indications, however, are that importations are still in excess of exportations by several million dollars. (P. 85)

The South African market for **perfumery** and **toilet preparations** is described. (Pp. 86–87)

Reconstruction in the **textile industries** in the northern district of France has advanced to such an extent that in some instances pre-war production has been exceeded. Before the war the dyeing of blue fabrics belonged almost exclusively to the Lille region, where the seven principal establishments used to treat annually an average of 100,000 pieces of 100 meters, with a turnover of 3,000,000 francs (about $600,000). These plants have resumed their pre-war leadership, with possibilities of still larger production. For bleaching, the Lille region rates two important establishments whose production will soon exceed the pre-war output, which in cotton and pure linen cloths amounted to about 500,000 pieces annually, with a 3,000,000-franc turnover. (P. 107)

The importation of **chlorate of potash** into China is prohibited. (P. 125)

The **salt industry** in Germany is described, the description including methods of production, producing regions, statistics showing the production during the period 1913–21, and its consumption and uses in Germany. (P. 159)

A company has recently been formed in Sweden for the exploitation, for use as a building material, of the large deposits of **kieselguhr.** This deposit differs from all others in that there is a natural intermixture of about 20 per cent bituminous products. A method has been perfected for the mechanical mass production of plates and of impregnating them through a simple and inexpensive process by which they will be completely impervious to moisture. The preliminary plans are to produce approximately 100,000 square meters of insulating plates annually, but to increase the production as soon as possible. (Pp. 166–67)

Lime production in Germany in 1922 totaled 4,354,000 tons, an increase of 306,000 tons or 7.5 per cent over that of 1921. (P. 167)

The production of **petroleum** in Italy has steadily declined during the past ten years. (P. 174)

Germany's production of **petroleum** in 1922 amounted to but 45,044 tons, or about 0.04 per cent of the world production; yet the 1922 estimate is higher than the figure for any year since 1916. (P. 174)

A free translation is given of the statement issued by the industrial experimental laboratory of the Mexican Department of Industry, Commerce, and Labor regarding the use of **sangre de drago** (**dragon's blood**) as a tanning extract. (P. 179)

The Canadian bill to amend the export act, providing that the Governor in Council may, by regulation, prohibit the exportation of **pulpwood** from Canada, was assented to by the Governor General on June 30. (Pp. 187–8)

Beginning with November 1 an import license must be obtained for the importation into France of all **benzenes, benzines, toluenes,** and spirits derived from **coal tar,** pure or mixed, gasoline and similar products, according to a decree of May 30, 1923. (P. 188)

The exportation of **sulfate of ammonia** from Tunis is subject to license. (P. 188)

Anthraquinone is exempted from import duty by a French decree. (P. 189)

Eight new **oil claims** have recently been denounced in Spain. Various other claims are in process of investigation. (P. 225)

The crude **mineral oil** production of Japan for 1922 was 1,860,032 barrels, a decrease of 14 per cent as compared with the year 1921. (P. 225)

The Hongkong **camphor** and **camphor oil** market is described. (Pp. 226–7)

A market for **petroleum products** exists in Germany. (Pp. 284–5)

The importance of American **sumac** to the American tanner is described. (Pp. 301–3)

The use of **chemical fertilizers** in South China has shown a marked increase in the past few years, the fertilizer most in demand being sulfate of ammonia. (P. 307)

The Chinese **wood-oil** situation is described. (P. 307)

STATISTICS OF EXPORTS TO THE UNITED STATES

Sweden—(P. 25)
  Wood pulp
Hongkong—(P. 38)
  Wood oil
East Prussia—(P. 198)
  Wood pulp
Netherlands—(P. 176)
  Beeswax
  Chemicals, drugs, dyes, etc.
  Fertilizers
  Gelatin
  Paints, colors, pigments, etc.

SPECIAL SUPPLEMENTS ISSUED

Brazil
Dutch East Indies
Paraguay
Syria
United Kingdom

Textile Industries of Belgium and the Netherlands. S. H. CROSS AND G. E. ANDERSON. *Trade Information Bulletin* 105.

CURRENT PUBLICATIONS

NEW BOOKS

Analytical Microscopy, Its Aims and Methods. T E Wallis. 149 pp Price, 6s. E. Arnold & Co., London.

Anleitung zur Organischen Qualitativen Analyse. H. Standinger. 94 pp. Price, 3s. Julius Springer, Berlin.

Atomic Structure and Spectral Lines. Arnold Sommerfield. Translated by Henry L. Brose. 626 pp. Illustrated. Price, $12.00. E. P. Dutton & Co., New York.

Chemische Technologie des Steinkohlenteers mit Berücksichtigung der Koksbereitung. Weissgerber. 141 pp. Price, 6s. Otto Spamer, Berlin.

Chemistry of the Inorganic Complex Compounds. An Introduction to Werner's Coördination Theory. R. Schwarz. Translated by L. W. Bass. 82 pp. Price, 8s. 6d. Chapman & Hall, Ltd., London.

Chemistry, Inorganic and Organic, with Experiments. C. L. Bloxam. 11th edition, revised by A. G. Bloxam and S. Judd Lewis. 832 pp. Price, 36s. J. & A. Churchill, London.

Designing, Construction, and Maintaining of Sewerage Systems and Sewage Treatment Plants. A. Prescott Folwell. 9th edition. 477 pp Illustrated. Price, $4.00. John Wiley & Sons, Inc., New York.

Determination of Hydrogen Ions. William Mansfield Clark. 2nd edition, revised and enlarged. 480 pp. Illustrated. Price, $5.00. Williams & Wilkins Co., Baltimore.

Elementary Physical Chemistry. W H. Barrett. 247 pp. Price, 6s. E. Arnold & Co., London.

Engineering Non-Ferrous Metals and Alloys. L. Aitchison and W. R. Barclay. 300 pp. Price, 21s. H. Frowde & Hodder & Stoughton, London.

Étude sur la Tannerie et les Industries Connexes au Maroc. Ch. Ziegler. 123 pp. Illustrated. Price, 7 fr. 50. La Chaussure Française, Paris.

Fire Losses—Locomotive Sparks. L. W. Wallace. 203 pp. Price, $3.00. Barr-Erhardt Press, Inc., New York.

Forest Resources of the World. Raphael Zon and William N. Sparhawk. 2 volumes. 997 pp. Illustrated. Price, $12.00. McGraw-Hill Book Co., Inc., New York.

Introduction to the Chemistry of the Cotton Industry. F. J. Cooper. 235 pp. Price, 10s. 6d Methuen & Co., Ltd., London.

Isotopes. A Damiens. 118 pp. Price, 12 fr. Gauthier-Villars & Cie, Paris.

Konstanten der Atomphysik. Edited by W. A. Roth, K. Scheel, and E. Regener. 114 pp. Price, 8s. 6d. Julius Springer, Berlin.

La Technique Industrielle des Parfums Synthétiques. R. Sornet. 135 pp. Price, 10 fr. Gauthier-Villars & Cie, Paris.

Light and Color in Advertising and Merchandising. M. Luckiesh. 284 pp. Illustrated. Price, $3.00. D. Van Nostrand Co., New York.

List of the Books, Bulletins, Journal Contributions, and Patents by Members of Mellon Institute of Industrial Research during the Calendar Year 1922. 11 pp. Mellon Institute, Pittsburgh.

Manufacture of Pulp and Paper. L. R. Benjamin. Bulletin No. 25, Institute of Science and Industry, Australia. 99 pp. Illustrated. Government Printer, Melbourne, Australia.

Microbiology. A Textbook of Microörganisms, General and Applied. C. E. Marshall 3rd edition, revised and enlarged. 1043 pp. Price, 21s. J. & A. Churchill, London.

Modern Gas Producers. N. E. Rambush. 545 pp. Price, 55s. Benn Bros., Ltd., London.

Organic Chemical Transformations. Lucius A. Bigelow and Kurwin R. Boyes. 4 pp. Price, 20 cents. **Coal Products Chart.** Alexander Lowy. Price, 15 cents. **An Outline for Qualitative Analysis.** Herbert O. Smith. 4 pp. Price, 10 cents. D. Van Nostrand Co., New York.

Perfumes and Cosmetics. William A. Poucher. 462 pp. Price, 21s. Chapman & Hall, Ltd., London.

Quantitative Chemical Analysis. Part I. Preparation of Inorganic Salts and Simple Exercise in Gravimetric and Volumetric Analysis. R. M. Caven. 153 pp. Price, 3s. 6d. Blackie & Son, Ltd., London.

Supplementary Notes on Gravimetric Analysis. W. Lowson 58 pp. Price, 2s. 6d. Longmans, Green & Co., London.

Shale Oils and Tars and Their Products. W. Scheithauer. 2nd edition, revised and enlarged by H. B. Stocks. 283 pp. Price, 12s. 6d. Scott, Greenwood & Son, London.

Trade Association Activities. L. E. Warford and Richard A. May. Department of Commerce Elimination of Waste Series. 368 pp. Price, 50 cents. Government Printing Office, Washington, D. C

Treatise on Chemistry. H. E. Roscoe and C. Schorlemmer. **Vol. II. The Metals.** New edition, revised. 1565 pp. Price, $15.00. Macmillan & Co., New York.

Varnishes, Their Chemistry and Manufacture. Ch. Coffignier. Translated by A H. J. Keane. 548 pp. Price, 21s. Scott, Greenwood & Son, London.

RECENT JOURNAL ARTICLES

Analyse des Papiers. André Beltzer. *L'Industrie Chimique*, Vol. 10 (1923), No. 114, pp. 298–301.

Assembling a Metallurgical Laboratory. Richard Rimbach. *Blast Furnace and Steel Plant*, Vol. **11** (1923), No. 8, pp. 419–23, 431.

Chemistry of the Acid Fixing Bath. S. E. Sheppard, Felix A. Elliott, and S. S. Sweet. *Journal of the Franklin Institute*, Vol. **196** (1923), No. 1, pp. 45–67.

Colouring of Metals. Alex. E. Tucker. *Journal of the Society of Chemical Industry*, Vol. **42** (1923), No. 28, pp. 299*t*–302*t*.

Degree of Dispersion as an Influence in Tanning. Jerome Alexander. *Journal of the American Leather Chemists Association*, Vol. **18** (1923), No. 8, pp. 400–9.

Depletion of Soil Phosphorus. Walter H. Voskuil. *American Fertilizer*, Vol. **59** (1923), No. 2, pp. 32–37.

Disintegration of Refractory Brick by Carbon Monoxide. B. M. O'Harra and W. J. Darby. *Journal of the American Ceramic Society*, Vol. **6** (1923), No. 8, pp. 904–14.

Effect of the Oxides of Arsenic on the Rate of Vulcanisation of Rubber. B. J. Eaton and R. O. Bishop. *Journal of the Society of Chemical Industry*, Vol. **42** (1923), No. 29, pp. 303*t*–7*t*.

Efficient Heating of Oil Fuel. Allen F. Brewer. *Industrial Management*, Vol. **66** (1923), No. 1, pp. 36–43.

Évolution des Industries de la Fermentation sous l'Influence des Théories de Pasteur. J. Effront. *Chimie et Industrie*, Vol. **9** (1923), No. 6, pp 1076–93.

Flow of Metal during Forging. L. A. Danse. *Forging and Heat Treating*. Vol. **9** (1923), No. 7, pp 304–07.

Further Studies on Cast Glass Pots. R. F. Geller and A. N. Finn. *Journal of the American Ceramic Society*, Vol. **6** (1923), No. 8, pp. 865–72.

Heat Balance of Carbonization Process. Julius K. Munster. *Blast Furnace and Steel Plant*, Vol. **11** (1923), No. 7, pp. 389–92.

Hydrogen Peroxide Bleaching. I. E. Weber. *Journal of the Society of Dyers and Colourists*, Vol. **39** (1923), No. 7 pp. 209–14.

Hydrolysis of Collagen by Trypsin. F. L. Seymour-Jones. *Journal of the Society of Leather Trades' Chemists*, Vol. **7** (1923), No. 7, pp. 293–304.

Influence of the Temperature at Which the Solution of Dyes Is Affected upon the Nature of the Solution. Walter C. Holmes. *Color Trade Journal*, Vol. **13** (1923), No. 2, pp. 54–56.

La Fixation Biologique de l'Azote de l'Air et la Solubilisation de l'Azote Organique par certaines Bactéries du Sol. Georges Truffaut. *Chimie et Industrie*. Vol. **9** (1923), No. 6, pp. 1094–1108.

Low Temperature Carbonization. V. Z. Caracristi. *American Gas Journal*, Vol. **119** (1923), No. 4, pp. 65–69, 76–78.

New Method of Magnetic Inspection. A. V. Deforest *Forging and Heat Treating*, Vol. **9** (1923), No. 7, pp. 296–300

Permanganate of Soda as a Bleaching Agent. William B. Nanson. *American Dyestuff Reporter*, Vol. **12** (1923), No. 16, pp. 556–60.

Physical Properties of Boric Oxide Containing Glasses and Their Bearing on the General Problem of the Constitution of Glass. S. English and W. E. S. Turner. *Journal of the Society of Glass Technology*, Vol. **7** (1923), No 26, pp. 155–69.

Relation between the Brightness and Hiding Power of White Paint Pigments. A. H. Pfund. *Journal of the Franklin Institute*, Vol. **196** (1923), No. 1, pp. 69–78.

Rubber from Evaporated Latex. O. E. De Vries. *India-Rubber Journal*, Vol. **66** (1923), No. 3, pp. 7–8

Silica Cement. E. N. McGee. *Journal of the American Ceramic Society*, Vol. **6** (1923), No 8, pp. 896–903.

Sur la Solidité des Matières Colorantes. Alfred Gillet and Fernand Giot. *Revue Generale des Matières Colorantes, de la Tenture, de l'Impression, et des Apprêts*, Vol. **28** (1923), No. 319, pp. 98–103.

Stainless Steels from the Point of View of the Glass Industry. W. H. Hatfield. *Journal of the Society of Glass Technology*, Vol. **7** (1923), No. 26, pp. 142–48.

Ultra-Filtration of Tannin and Other Solutions. R. Jay Browne. *Journal of the American Leather Chemists Association*, Vol. **18** (1923), No. 8, pp. 409–23

Use of Light in Metallography. Robert E Guthrie. *Forging and Heat Treating*, Vol. **9** (1923), No. 6, pp. 263–68.

Valuation of Dyestuffs by Titration Methods. Reginald B Brown and Harold Jordan. *Journal of the Society of Dyers and Colourists*, Vol. **39** (1923), No. 7, pp. 203–9.

Year in Review in the World of Glass Technology. W. E. S. Turner. *Journal of the Society of Glass Technology*, Vol. **7** (1923), No. 26, pp. 132–41.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Corrosion: A. C. P. Metal Treating Products and Processes. A 24-page descriptive catalog of the products of the American Chemical Paint Co., Philadelphia.

Power: The Coxe Stoker. An 8-page bulletin descriptive of this type of stoker. Published by the Combustion Engineering Corp., 43 Broad St., New York.

Vitamins: The Distribution of Vitamins in Nature. William D. Richardson. Bulletin No. 5 of the Institute of Margarin Manufacturers, Washington, D. C.

GOVERNMENT PUBLICATIONS

***Notice**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Comparative Tests of By-Product Coke and Other Fuels for House-Heating Boilers. Henry Kreisinger, John Blizard, H. W. Jarrett, and J. J. McKitterick. *Technical Paper* **315.** 21 pp. Paper, 5 cents.

Explosives Used in May, 1923. W. W. Adams. *Reports of Investigations* **2501.** 6 pp. Issued July, 1923.

Gases Liberated by High-Voltage Insulator Testing Apparatus. G. W. Jones and W. P. Yant. *Reports of Investigations* **2497.** 4 pp. Issued July, 1923.

Mine Rescue Standards. A Tentative Study. Prepared by a committee appointed at the International Mine-Rescue Standardization Conference, September, 1921. *Technical Paper* **334.** 43 pp. Paper, 5 cents.

Oxygen-Oil Explosions. Preliminary Report I. General Outline of the Problem and Summary of Results to Date. M. D. Hersey. *Reports of Investigations* **2507.** 9 pp. Issued July, 1923.

Platinum Assays and Platinum Promotions. S. C. Lind, C. W. Davis, and M. W. von Bernewitz. *Reports of Investigations* **2496.** 21 pp Issued July, 1923.

Bureau of Standards

Invar and Related Nickel Steels. *Circular* **58,** 2nd ed. Paper, 30 cents.

Recommended Specifications for Limestone and Quicklime for Use in the Manufacture of Sulfite Pulp. *Circular* **144.** Paper, 5 cents.

Recommended Specification for Quicklime for Use in Causticizing. *Circular* **143.** Paper, 5 cents.

Congress

High Cost of Gasoline and Other Petroleum Products. Hearings before subcommittee pursuant to S. Res. 295 amending S. Res. 292, directing the Committee on Manufactures to investigate and report to the Senate the conditions of crude oil and gasoline markets during the years 1920, 1921, and to date in 1922. 943 pp. (These hearings were also issued in separate numbered parts. The chronology and index were also published separately.)

Department of Agriculture

Determination of Fatty Acids in Butter Fat. II. E. B. Holland, M. E. Garvey, H. B. Pierce, A. C. Messer, J. G. Archibald, and C. O. Dunbar. *Journal of Agricultural Research*, **24** (May 5, 1923), 365–98.

Nutritive Value of the Georgia Velvet Bean (Stizilobium Deeringianum). J. W. Read and Barnett Sure. *Journal of Agricultural Research*, **24** (May 5, 1923), 433–40.

Oxidation of Sulfur by Microörganisms in Black Alkali Soils. S. A. Waksman, Jacob Joffe, and R. L. Starkey. *Journal of Agricultural Research*, **24** (April 28, 1923), 297–306.

Toxicity and Antagonism of Various Alkali Salts in the Soil. F. S. Harris, M. D. Thomas, and D. W. Pittman. *Journal of Agricultural Research*, **24** (April 28, 1923), 317–38.

Federal Trade Commission

Report of the Federal Trade Commission on the Calcium Arsenate Industry. March 3, 1923. *Senate Document* **345.** 21 pp. Paper, 5 cents.

Geological Survey

Asphalt and Related Bitumens in 1922. K. W. Cottrell. Separate from Mineral Resources of the United States, 1922, Part II. 7 pp. Issued July 19, 1923.

Bismuth, Selenium, and Tellurium in 1922. V. C. Heikes. Separate from Mineral Resources of the United States, 1922, Part I. 11 pp. Published July 16, 1923.

Ilsemannite at Ouray, Utah. F. L. Hess. *Bulletin* **750-A.** Separate from contributions to Economic Geology, 1923, Part I. 16 pp. Published June 28, 1923.

Lead and Zinc Pigments and Salts in 1922. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1922, Part I. 9 pp. Published July 25, 1923.

Lead in 1922. General Report. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1922, Part I. 10 pp. Published July 17, 1923.

Mineral Resources of the United States in 1920. Part I. Introduction. G. F. Loughlin. 151 pp. Issued July, 1923.

Progress Report on a Subsurface Study of the Pershing Oil and Gas Field, Osage County, Oklahoma. W. W. Rubey. *Bulletin* **751-B.** Separate from Contributions to Economic Geology, 1923, Part II. 48 pp. Published July 18, 1923.

Surface Water Supply of the United States, 1919-1920. Part I. North Atlantic Slope Drainage Basins. N. C. Grover, C. H. Pierce, C. C. Covert, O. W. Hartwell, and G. C. Stevens. Prepared in coöperation with the States of Maine, New Hampshire, Vermont, Massachusetts, Connecticut, New York, and Pennsylvania. *Water-Supply Paper* **501.** 330 pp. Paper, 30 cents.

Surface Water Supply of the United States, 1919 and 1920. Part XII. North Pacific Slope Drainage Basins. A. Pacific Basins in Washington and Upper Columbia River Basin. N. C. Grover, G. L. Parker, and W. A. Lamb. Prepared in coöperation with the States of Washington, Montana, and Idaho. *Water-Supply Paper* **512.** 262 pp. Paper, 25 cents.

Surface Water Supply of the United States, 1919-1920. Part X. The Great Basin. N. C. Grover, A. B. Purton, H. D. McGlashan, F. F. Henshaw, C. G. Paulsen, and Robert Follansbee. Prepared in coöperation with the States of Utah, Nevada, California, Oregon, Wyoming, and Idaho. *Water-Supply Paper* **510.** 348 pp. Paper, 30 cents.

The Lime Belt of Massachusetts and Parts of Eastern New York and Western Connecticut. T. N. Dale. *Bulletin* **744.** 71 pp. Paper, 30 cents

Zinc in 1922. C. E. Siebenthal and A. Stoll. Separate from Mineral Resources of the United States, 1922, Part I. 16 pp. Published July 18, 1923.

National Advisory Committee for Aeronautics

An Airship Slide Rule. E. R. Weaver and S. F. Pickering. *Report* **160.** 12 pp.

Public Health Service

Indicators for pH Control of Alum Dosage. Barnett Cohen. *Reprint* **828** from *Public Health Reports.* 4 pp. Paper, 5 cents.

Intensive Localized Distribution of the Spore of B. Botulinus and Probable Relation of Preserved Vegetables to Type Demonstrated. J. C. Geiger and Harriet Benson. *Public Health Reports* **38** (July 20, 1923), 1611–5.

Present Status of Sanitary Engineering. Suggestions for Objects and Aims of the Sanitary Engineering Division of the American Society of Civil Engineers. H. P. Eddy. *Reprint* **831** from *Public Health Reports.* 13 pp. Paper, 5 cents.

Standardization of Insulin. I. Toxicity of Insulin for White Rats as Influenced by Temperature of Room in Which Animals Are Kept. Carl Voegtlin and E. R. Dunn. *Public Health Reports* **38** (August 3, 1923), 1747–9.

Studies on Oxidation-Reduction. I. Introduction. W. M. Clark. *Reprint* **823** from *Public Health Reports.* 12 pp. Paper, 5 cents.

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Studies on Oxidation-Reduction. IV. Electrode Potentials of Indigo Sulfonates, Each in Equilibrium with Its Reduction Product. M. X. Sullivan, Barnett Cohen, and W. M. Clark. *Public Health Reports* **38** (July 27, 1923), 1669–1718.

Studies on the Bio-Assay of Pituitary Extracts Concerning the Use of a Desiccated Infundibular Powder as a Standard in the Physiological Evaluation of Pituitary Extracts. M. I. Smith and W. T. McClosky. *Reprint* **822** from *Public Health Reports.* 22 pp. Paper, 5 cents.

Smithsonian Institution

Some Practical Aspects of Fuel Economy. C. W. Mitman. *Publication* **2715.** 19 pp. June 2, 1923.

MARKET REPORT—AUGUST, 1923

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

Although there has been some spasmodic buying of chemicals in a small way during the month, price movements, where they have not become stagnated at low levels, were downward in the big majority of cases. Quotations for all groups of chemicals, coal-tar products, oils, and allied products reached the lowest point of the year during August. With numerous prices quoted below production costs, and each sale representing a loss, sellers have gradually built up a resistance to further price shading during the month. Rather than take too great a loss on goods which are held in storage, sellers who are financially able are withdrawing from the market. The chemical market, as a whole, has become thoroughly disorganized, which condition can be traced back directly to large operations by financially weak importers throughout four months of a falling market.

Usual summer dullness and a waiting policy on the part of buyers holds business at a minimum. The first part of August was reported somewhat better than that of July, but far from satisfactory from sellers' point of view. Prices of domestic chemicals have now assumed a tendency to decline while imported materials have steadied slightly, especially those of German origin. Uncertainty of the future continues to keep buyers marking time in purchasing and they have been taking only enough for immediate requirements. This procedure has developed the keenest type of competition among dealers, while manufacturers have been shading prices as well to get the business.

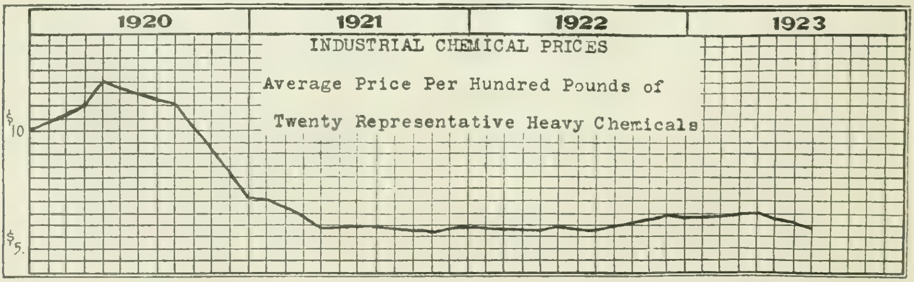
Alkalies have been a steady feature in the market. Manufacturers of caustic soda and soda ash report business slightly above normal for this season of the year, with prices on a stable basis. The increased cost of production has been offset by the increased volume of business this year and makers are reluctant to increase prices. Rumors of a price war in the fall are without foundation according to producers. Demand for heavy acids has been moderate at unchanged prices. Oxalic acid is easier. Bleaching powder has been in an unsettled state owing to a slow summer demand and keen competition among makers and dealers. Some dealers have been quoting below manufacturers' prices. Chlorine has been subject to price shading. Bichromates have been declining gradually owing to a continued lack of demand and keen competition between makers. Demand for copper sulfate has quieted down and prices are easier owing to weakness in the metal. Imported sodium prussiate has recovered from its slump and is quoted higher, while domestic makers have reduced prices to meet the competition. Barium compounds are firmer, especially the imported products.

Domestic production of potassium permanganate has been started with prices slightly higher than the imported material. Potassium chlorate has been in good demand and prices are higher. Imported caustic potash is steady with shipment prices slightly higher. Domestic is unchanged. Yellow potassium prussiate is steady while the red variety is lower. Mercury has declined to \$63.00 to \$64.00 per flask owing to a weakening in the London market. Tin crystals were unchanged during August, while tin oxide was lower.

Arsenic and calcium arsenate continue weak at a time when the market should be strong. The lack of demand for arsenate has been very disappointing to the dealers in this commodity. Early estimates predicted that there would be a shortage of arsenate this year and dealers in the South and North stocked up in anticipation of an active demand when the boll weevil began its attack on the cotton plants. Owing to a dry season in the South, the boll weevil did not appear in great numbers this year, and much arsenate has been left in the hands of dealers, who have been anxious to dispose of their stocks at almost any price. Prices have dropped to 11 or 12 cents per pound from earlier quotations of 16 and 17 cents per pound. Toward the middle of the month a demand for arsenate and Paris green developed owing to the appearance of large numbers of cotton leaf worms.

The situation on coal-tar products has improved during the summer months. Supplies are more plentiful and prices are easier to meet than those recently prevailing. Open market prices for phenol have been close to 30 cents per pound, while two domestic makers of synthetic phenol are quoting 35 cents per pound at works. Cresylic acid has also declined and pale material has been sold from 75 to 85 cents per gallon. Demand for these products has not been active, however. Benzene and toluene are lower owing to a larger stock in sellers' hands. Naphthalene has been quiet. Pyridine has been scarce and prices are holding at high levels. Intermediates and coal-tar dyes have been very quiet. Prices of intermediates remain steady, while dyestuff prices are subject to shading. A domestic maker of synthetic indigo announced an advance from 22 to 26 cents per pound in car lots.

With the future uncertain, buyers are not anticipating their requirements and are only purchasing oils for their immediate needs. Linseed oil has been declining steadily and is now below the \$1.00 level. China wood oil is holding steady owing to the small offerings from China and meager stocks on spot. Menhaden oil has been yielding to the lack of buying interest and operators in the Chesapeake district have reduced their prices. Buyers are still holding off waiting for lower prices. Cod oil has been declining gradually. Salicylic acid is lower owing to keen competition among manufacturers. Prices appear to be stabilized at 35 cents per pound, which is the same price quoted for phenol.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

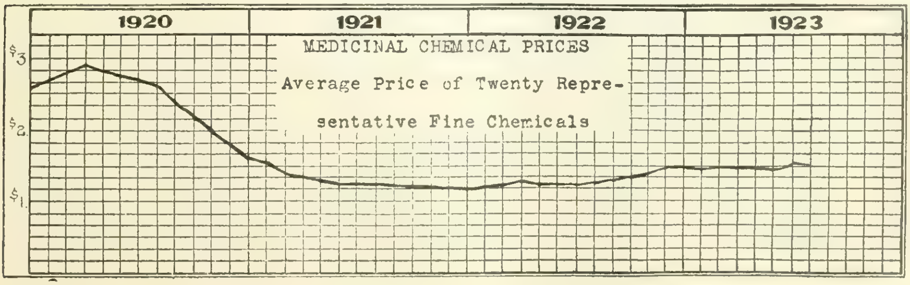
	Aug 1	Aug 15	Jan 1923
Acid, Boric, cryst. bbls.......lb.	.11	.11	.11½
Hydrochloric,comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb.	.65	.65	.65
Nitric, 42°, cbys. c/1 wks.lb.	.05¾	.05¾	.06
Phosphoric, 50% tech....lb.	.08	.08	.08
Sulfuric, C. P...........lb.	.09	.09	.07
66° tks. wks.......ton	15.00	15.00	15.00
Oleum, 20%.......ton	19.00	19.00	18.00
Alum, Ammonia, lump.......lb.	.03½	.03½	.03½
Potash, lump...........lb.	*.03¼	*.03¼	*.03½
Chrome.............lb.	.05½	.05½	.05½
Soda, ground...........lb.	.04	.04	.04
Aluminum Sulfate (iron-free) .lb.	.02½	.02¼	.02½
Ammonium Carbonate, pwd..lb.	.09	.09	.09½
Chloride, white gran.....lb.	.07½	.07½	.07½
Ammonia, anhydrous........lb.	.30	.30	.30
Ammonia Water, drums, 26°.lb.	.07½	.07½	.07½
Arsenic, white..............lb.	.09	.10	.15½
Barium Choride............ton	*80.00	*82.50	*92.50
Nitrate.................lb.	*.07¾	*.07¾	*.07½
Barytes, white.............ton	33.50	33.50	33.50
Bleaching Powd., 35%, works .... 100 lbs.	1.75	1.75	2.15
Borax, cryst., bbls...........lb.	.05½	.05¼	.05½
Bromine, pure, wks..........lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b. N. Y...................ton	24.50	24.50	24.50
Chlorine, liquid.............lb.	.05¼	.05¼	.05¼
Copper Sulfate......... 100 lbs.	5.35	5.25	6.25
Iodine, resublimed..........lb.	4.55	4.55	4.50
Lead Acetate, white crystals..lb.	.14	.14	.13
Nitrate.................lb.	.22	.22	.22
Red.............. 100 lbs.	11.40	11.40	10.60
White (Carb.)..........lb.	.09¾	.09¾	.08½
Lime, live and hydrated, bbl..lb.	.01½	.01½	.01½
Oyster shell............lb.	.03	.03	.03
Lime Acetate.......... 100 lbs.	4.00	4.00	3.50
Magnesium Carbonate, tech..lb.	.08	.08	.08
Magnesite, calcined.........ton	55.00	55.00	55.00
Phosphorus, yellow..........lb.	*.35	*.35	*.28
Red...................lb.	—	—	*.30
Plaster of Paris, tech ....bbl.	3.30	3.30	3.30
Potassium Bichromate.......lb.	.10¼	.10⅛	.10
Bromide, imported......lb.	.17	*.16½	.14½
Carbonate, calc.,80–85%.lb.	*.06½	*.06½	*.05½
Chlorate, cryst..........lb.	*.07	*.07	*.05½
Hydroxide, 88–92%.....lb.	*.07½	*.07½	*.08
Iodide, bulk, U. S. P.....lb.	3.75	3.75	3.60
Nitrate................lb.	.06½	.06½	.06½
Permanganate, U. S. P...lb.	*.16½	*.17	*.16
Prussiate, red...........lb.	*.63	*.63	*.90
Yellow.............lb.	*.35	*.35	*.38
Salt Cake, bulk.............ton	26.00	26.00	28.00
Silver Nitrate...............oz.	.44½	.44½	.44
Soda Ash, 58%, bags....100 lbs.	*2.00	*2.00	*2.00
Caustic, 76%, N. Y. 100 lbs.	3.70	3.70	3.50

	Aug. 1	Aug. 15	Jan. 1923
Sodium Acetate.............lb.	.05½	.05	.07¼
Bicarbonate....... 100 lbs.	2.25	2.25	2.00
Bichromate.............lb.	.08	.08	.07¾
Bisulfite, powd..........lb.	.04	.04	.04
Chlorate................lb.	.06½	.06½	.06½
Cyanide, 96–98%.......lb.	.23	.23	.23
Fluoride, tech...........lb.	.09½	.09½	.09½
Hyposulfite, bbls... 100 lbs.	2.90	2.90	3.60
Nitrate, 95%...... 100 lbs.	2.42½	2.42½	2.57½
Nitrite..................lb.	.07¼	.07¼	.08½
Prussiate, yellow........lb.	.13½	.14	.18½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40° ....100 lbs.	.80	.80	.80
Sulfide, 60%, fused......lb.	.05	.05	.05
Strontium Nitrate...........lb.	*.10	*.10	*.08¾
Sulfur, flowers.........100 lbs.	3.00	3.00	3.00
Crude, mines......long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n....lb.	.11½	.11½	.10¼
Oxide..................lb.	.45	.45	.43
Zinc Chloride, U. S. P........lb.	.25	.25	.20
Oxide, bbls.............lb.	.08½	.08½	.07½

ORGANIC CHEMICALS

	Aug. 1	Aug. 15	Jan. 1923
Acetanilide, U. S. P., bbls....lb.	.35	.32	.35
Acid, Acetic, 28 p. c.... 100 lbs.	3.38	3.38	3.17½
Glacial ....100 lbs.	12.78	12.78	12.05
Benzoic, U. S. P.........lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drums..............lb.	.35	.35	.32
50- to 110-lb. tins...lb.	.35	.35	.34
Citric, crystals, kegs.....lb.	*.50½	*.50	*.48½
Oxalic, cryst., bbls., wks.lb.	.12¼	.12¼	.13½
Pyrogallic, resublimed...lb.	1.55	1.55	1.55
Salicylic, U. S. P.........lb.	.35	.35	.45
Tannic, U. S. P., bbls....lb.	.83	.83	.70
Tartaric, cryst., U. S. P...lb.	*.34	*.34	*.32
Acetone, drums..............lb.	.25	.25	.21
Alcohol,denatured, complete. gal.	.46	.46	.45
Ethyl, 190 proof, bbls...gal.	4.75	4.75	4.70
Amyl Acetate.............. gal.	4.50	4.50	2.50
Camphor, Jap, refined, cases .lb.	.87	.87	.86
Carbon Bisulfide, c/1........lb.	.06¾	.06¾	.06¾
Tetrachloride...........lb.	.10½	.10½	.10½
Chloroform, U. S. P., drums..lb.	.35	.35	.35
Creosote, U. S. P............lb.	.50	.50	.40
Cresol, U. S. P...............lb.	.36	.36	.25
Dextrin, corn ....100 lbs.	3.79	3.79	3.09
Imported Potato........lb.	.07	.07	.09
Ether, U. S. P., 100 lbs.......lb.	.13	.13	.13
Formaldehyde, bbls..........lb.	.14	.14	.16
Glycerol, dynamite, drums...lb.	.15½	.16	.16½
Methanol, pure, drums......gal.	1.30	1.30	1.35
Methylene Blue, med........lb.	2.25	2.25	2.25
Petrolatum, light amber......lb.	.04½	.04½	.03¾
Pyridine ....gal.	4.00	4.25	2.75
Starch, corn, pow'd.....100 lbs.	3.22	3.22	2.47
Potato, Jap.............lb.	.05	.05	.06¾
Sago....................lb.	.04½	.04½	.03½

* Resale or Imported (not an American maker's price).



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Aug. 1	Aug. 15	Jan. 1923
Beeswax, pure, white ....lb.	.37	.37	.36
Castor Oil, No. 3............lb.	.13½	.13	.13
Ceresin, yellow..............lb.	.08	.08	.08½
Corn Oil, crude, tanks, mills...lb.	.07¾	.07¾	.09¾
Cottonseed Oil, crude, f. o. b. mill...................lb.	—	—	.09⅝
Linseed Oil, raw, lc/l........gal.	1.00	.97	.87
Menhaden Oil, crude, mills...gal.	.40	.40	.53
Neat's-foot Oil, 20°..........lb.	.16¾	.17½	.18½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	6.00	5.95	6.25
Rosin Oil, first run..........gal.	.45	.45	.45
Shellac, T. N................lb.	.54	.57	.80
Sperm Oil, bleached winter, 38°...................gal.	.99	.99	1.03
Stearic Acid, double pressed...lb.	.13	.13	.12½
Tallow Oil, acidless..........lb.	.10½	.10	.11½
Turpentine, spirits of........gal.	.98	.95	1.56

METALS

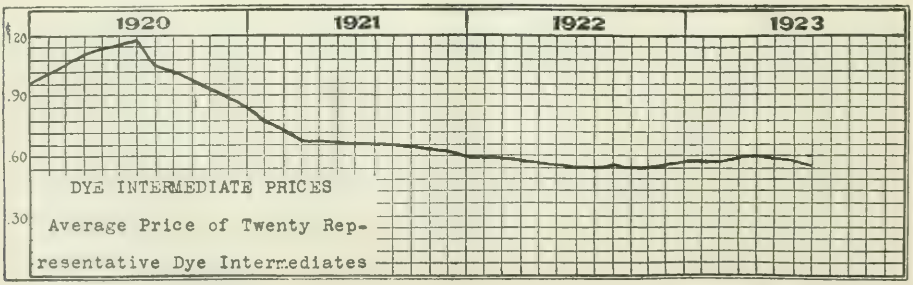
	Aug. 1	Aug. 15	Jan. 1923
Aluminium, No. 1, ingots.....lb.	.25	.25	.23
Antimony, ordinary......100 lbs.	6.75	6.75	6.75
Bismuth.....................lb.	2.75	2.75	2.75
Copper, electrolytic..........lb.	.14⅝	.14⅛	.14¾
Lake..................lb.	.14⅞	.14⅜	.14¾
Lead, N. Y.............100 lbs.	6.50	6.50	7.80
Nickel, electrolytic...........lb.	.29	.29	.36
Platinum, refined, soft........oz.	116.00	116.00	118.00
Quicksilver, flask......75 lbs. ea.	65.00	64.00	73.00
Silver, foreign...............oz.	.63½	.63⅛	.63
Tin........................lb.	.38¾	.38⅛	.39
Tungsten Wolframite....per unit	8.50	8.50	7.50
Zinc, N. Y.............100 lbs.	6.65	6.55	8.25

FERTILIZER MATERIALS

	Aug. 1	Aug. 15	Jan. 1923
Ammonium Sulfate, expt.100 lbs.	3.40	3.45	3.90
Blood, dried, f. o. b. N. Y...unit	3.75	3.75	4.70
Bone, 3 and 50, ground, raw..ton	28.00	25.00	28.00
Calcium Cyanamide, unit of ammonia..................	2.25	2.25	2.25
Fish Scrap, dried, wks.......unit	3.75	3.75	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.25	3.25	3.00
Florida, 70%...........ton	3.55	3.55	3.55
Florida, 74–75%........ton	4.50	4.50	4.50
Tennessee, 72%.........ton	5.50	5.50	5.25
Potassium Muriate, 80%....unit	.68	.68	.68
Tankage, high-grade, f. o. b. Chicago...............unit	3.60 & .10	3.60 & .10	4.75 & .10

COAL-TAR CHEMICALS

Crudes	Aug. 1	Aug. 15	Jan. 1923
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.25	.25	.30
Naphthalene, flake...........lb.	.07½	.07½	.06½
Phenol, drums...............lb.	.35	.35	.32
Crudes *(concluded)*			
Toluene, pure, tanks.........gal.	.28	.28	.30
Xylene, 2 deg. dist. range, drums.................gal.	.65	.65	—
Intermediates			
Acids:			
Anthranilic..............lb.	.96	.96	1.10
Benzoic, tech............lb.	.70	.70	.65
Cleve's..................lb.	1.00	1.00	1.25
Gamma...................lb.	1.70	1.70	1.85
H.......................lb.	.75	.75	.80
Metanilic...............lb.	.60	.60	.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.62	.62	.60
Nevile & Winther's.......lb.	1.25	1.25	1.15
Picric...................lb	.25	.25	.20
Sulfanilic...............lb.	.20	.20	.19
Tobias'.................lb.	1.30	1.30	1.30
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil.................lb.	.17	.17	.17
Aniline Salt................lb.	.24	.24	.25
Anthraquinone (sublimed).....lb.	1.30	1.30	1.30
Benzaldehyde, tech...........lb.	.75	.75	.65
U. S. P..................lb.	1.50	1.50	1.40
Benzidine Base..............lb.	.82	.82	.84
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol...............lb.	3.80	3.80	3.75
Dianisidine.................lb.	4.60	4.60	4.50
p-Dichlorobenzene...........lb.	.17	.17	.17
Diethylaniline...............lb.	.60	.60	.60
Dimethylaniline..............lb.	.42	.41	.41
Dinitrobenzene..............lb.	.19½	.19½	.19
Dinitrotoluene...............lb.	.19	.19	.20
Diphenylamine...............lb.	.48	.48	.50
G Salt......................lb.	.55	.55	.60
Hydroquinol.................lb.	1.25	1.25	1.05
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist............lb.	.22	.22	.26
a-Naphthylamine............lb.	.35	.35	.29
b-Naphthylamine............lb.	.75	.75	.95
m-Nitroaniline..............lb.	.78	.78	.80
p-Nitroaniline..............lb.	.74	.74	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol..............lb.	1.00	1.00	.72
o-Nitrotoluene..............lb.	.10	.10	.10
p-Nitrotoluene..............lb.	.60	.60	.65
m-Phenylenediamine.........lb.	.98	.98	1.00
p-Phenylenediamine.........lb.	1.45	1.45	1.50
Phthalic Anhydride..........lb.	.30	.30	.35
R Salt......................lb.	.55	.55	.55
Resorcinol, tech.............lb.	1.50	1.50	1.50
U. S. P..................lb.	2.00	2.00	2.00
Schaeffer's Salt.............lb.	.60	.60	.60
Sodium Naphthionate........lb.	.62	.62	.62
Thiocarbanilide..............lb.	.35	.28	.35
Tolidine (base)..............lb.	.95	.95	.95
Toluidine, mixed............lb.	.31	.31	.30
o-Toluidine.................lb.	.15	.15	.15
p-Toluidine.................lb.	.90	.90	1.00
m-Toluylenediamine.........lb.	.90	.90	.95
Xylidine....................lb.	.50	.50	.42



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EDITORIALS

The Prize Essay Contest

CHEMISTS have a splendid opportunity for service in carrying out the details of the prize essay contest made possible by a gift on the part of Mr. and Mrs. Francis P. Garvan to encourage the study of chemistry so that the youth of the land may appreciate what the science is doing for our everyday life. Six topics have been chosen by the committee, and the first prize of a twenty dollar gold piece with a certificate will be awarded in each state and the District of Columbia for the best essay within these geographical areas on each topic. Undoubtedly, efforts will be made within the various states to provide inducements for further study in the form of scholarships in the institutions of higher education. From among the state winners a national committee, to be announced later, will select the winners to receive the four-year scholarships at Yale or Vassar. These scholarships carry $500 a year and tuition, and were made possible by the generosity of Mr. and Mrs. Garvan.

This is not all the story, for to insure access to suitable literature, the reading of which will stimulate the imagination of contestants and indicate methods of attacking their problem, Mr. Garvan has provided for the distribution of more than ten thousand sets of five books each, these to be sent to the accredited secondary schools, both public and private, without so much as a request. A number of sets will also be deposited with libraries prepared to facilitate their circulation, and we prophesy that the coming winter will see a wider demand for and a more extensive reading of popular literature on chemical subjects than ever before. We all recognize that in the boys and girls lies our greatest opportunity to encourage chemistry. This does not mean that we expect all high and secondary school students to become chemists. It does mean that attention will be drawn to chemistry as a cultural study, that a wider view upon everyday affairs will be obtained, and that chemistry will be placed in the popular estimation, on a par with astronomy, for example, which has obtained a big hold upon the layman.

This is the first nation-wide plan of this kind to be evolved. In accepting its administration the SOCIETY has assumed a real responsibility. It is a call to the individual chemist as well as to the organized sections to recognize their responsibility in the successful completion of the work. Everything possible is being done to bring the contest before the boys and girls, and we must expect frequent calls for assistance in recommending literature, sometimes in discussing the chemical work, and perhaps in arranging for visits to plants utilizing chemistry in some of its phases. There will doubtless also be a large number of essays to be seriously considered in the competition. In fact, it is difficult to predict all the ways in which some service may be required. While the prizes are to be awarded to students of high school grade, much of the benefit of the contest will eventually accrue to chemists and their science. We therefore have a direct interest in the success of the contest.

A prize essay committee has been organized, with the secretary equipped to handle inquiries which chemists and others may care to make. There will be ample explanatory literature for distribution, and it is hoped that adequate and proper publicity for our effort may be obtained. It is another opportunity for chemists to show the value of their organization. The work at its inception holds promise of marked success.

The American Chemical Prize

WHEN Dr. Smith announced at Pittsburgh that the Allied Chemical and Dye Corporation through William H. Nichols as spokesman had founded an annual prize of $25,000, the Council wisely chose a committee consisting of Edgar F. Smith, E. W. Morley, C. F. Chandler, F. P. Venable, and Ira Remsen, to collaborate with representatives of the corporation in arranging the necessary details. Shortly before the New Haven meeting the death of Dr. Morley was announced and Theodore W. Richards has taken his place upon the committee. The committee was not ready to report at New Haven and the Council eagerly awaited its report at Milwaukee. The magnificent prize will be known as

THE AMERICAN CHEMICAL PRIZE

(*Founded by the Allied Chemical and Dye Corporation*)

and "will be awarded annually to that chemist, man or woman, a citizen or resident of the United States of America at the time, who in a certain year or through a period of years has made a contribution of high merit or in some marked way has promoted the betterment of society through the science of chemistry."

Our committee is to designate the additional members of the AMERICAN CHEMICAL SOCIETY upon the jury of award, and as soon as this jury can be completed and agree upon recommendations the first recipient of the prize will be announced. This recognition of outstanding work in chemistry cannot fail to benefit chemistry in America to a degree in comparison with which the monetary reward to the chemist is insignificant. Somehow, for the encouragement of the large number of chemists who now work faithfully in obscure places, we hope the first to receive this prize will be some one who has labored in a little-known laboratory with inadequate facilities. We should like to see it demonstrated that a man with native ability and steadfast purpose can achieve things even though he does not have the advantages obtained in large institutions and centers of population. We should also like to see one of the younger men encouraged in his work, as an indication that the prize is not to go necessarily to the older members of the profession and to dispel the idea that in addition to outstanding work a man must attain years before he can win full recognition.

Long after those who have been instrumental in the foundation of this annual prize have passed on, the science and the general public will continue to reap the harvest. The thanks of chemists are properly due to William H. Nichols, a past president of our SOCIETY, an honorary member, and the recipient of many scientific honors, who has acted as spokesman for the Allied Chemical and Dye Corporation in this matter. As for our committee, nothing that can be said here would add to the frequent expressions of the debt of gratitude that American chemists owe the members of the committee for their continued work which has done so much in the past, as in the present, to bring chemistry to the forefront and maintain America's position as a nation unsurpassed in its modern chemical achievement.

In Duncan's Footsteps

ACCORDING to the best of our information it was the late Robert Kennedy Duncan who, in modern times, emphasized the necessity of popularizing our science in order to win that sympathetic appreciation on the part of the public which we must have if fundamental research and even the industrial application of its results is to have support upon an adequate scale. The "Chemistry of Commerce" and other works by Duncan are classics, and form the nucleus of a growing series of publications which are not only valuable to us as chemists, but which have attracted so wide a circle of nontechnical readers as to make them commercially attractive to the publishers.

Interest in the popularization of science on the part of those charged with public responsibility is manifest in the message upon the cover of our September issue, which was especially prepared for *Industrial and Engineering Chemistry* by the Secretary of Commerce, and shows an appreciation for science which until lately has been unique among public men.

The women of the country are becoming increasingly interested in the application of science to everyday life. Those who heard Mrs. Winter at the General Meeting at Milwaukee could not fail to be impressed by her plea for further simplification of scientific facts to facilitate their assimilation by the intelligent lay reader. She offered the coöperation of the efficient organizations of American women if chemists will do their part in preparing the results of their labors, their plans for the future, and statements concerning the significance of their work, so they may be comprehended without previous training in the science.

The newspapers must consider the desire of the public in preparing copy for their numerous editions, and subjects not considered news are practically debarred from their columns. We doubt if any organization has ever obtained more desirable space in first-rate newspapers than was accorded the AMERICAN CHEMICAL SOCIETY in connection with the Milwaukee meeting. We seem to have passed the stage when a few inches tucked away on an inconspicuous page was considered adequate by the editor. We are frequently given preferred space, and our stories are carried on different pages of the same edition.

We, who are committed to the popularization of our science through the publication of authentic but nontechnical articles, are further encouraged by the steadily changing attitude of those who confine their efforts to researches in pure science. In this group are the representatives of sciences other than chemistry who have come to realize that, to some extent at least, the present position of chemistry in America is due to the willingness of even our most renowned chemists to have the public understand their work.

All of which means that something is happening. The public is asking for chemical information. The daily press is making a greater effort to study that demand, and the extent to which we may go in securing publicity depends wholly upon the coöperation which the chemist gives, not only to our A. C. S. News Service, our News Edition, and the publicity committees of local sections, but to the individual reporter bent upon serious inquiry. Sometimes we cannot approve the headlines employed, but these are becoming more satisfactory and, after all, are not so objectionable as would be an omission of authentic chemical information from the daily press.

We have established an enviable reputation in the popularization of science and our influence can be greatly extended with your hearty coöperation.

An Appeal for Opinions

TIME after time the Council of the SOCIETY creates a committee of busy men and charges them with the duty of formulating plans or making decisions upon questions of vital interest to the life and growth of our organization. Having created the committee, members of the SOCIETY forget their responsibility in its work, and as a consequence may be disappointed in the committee's report when it appears. We know that in many localities men are devoting a great deal of thought to questions now before the SOCIETY, but for some unexplained reason results of their deliberations are too seldom registered with those who endeavor to serve the SOCIETY. We wish to appeal to sections and individuals to send their criticisms and suggestions to the committees seeking information. Two of the committees continued—namely, those on intersectional meetings and the classification of membership—have before them questions which merit prolonged discussion. These questions should be discussed by the local sections and their recommendations transmitted through the executive committees. In no other way will committees be able to discharge their duty as they see it and perform the service which they desire to render. There are more than sixty-five sections in the AMERICAN CHEMICAL SOCIETY, and the Committee on Intersectional Meetings has heard from but twenty-nine. The Committee on Prize Essays has also appealed to various local sections for recommendations with respect to the personnel of state committees and other details. The response has been far from complete.

These and other questions should be placed upon the program of each local section for early consideration and discussion. Do not let the matter end with discussion. By all means transmit to the appropriate committee or individual specific opinions containing suggestions along definite lines and, where possible, complete plans for consideration. In the case of questions requiring sectional action, communications should be official and not merely the expression of individual ideas.

Earning Power of Research

ORIGINALLY, the lead from which cable sheaths are made was given a 3 per cent admixture of tin to obtain the necessary mechanical properties in the alloy. About twelve years ago the price of tin advanced, while the increase in the quantity required for new telephone cable construction became so large that research was called upon to provide a substitute. As a result new sheaths contain one per cent of antimony and in ten years the new formula has earned a saving approximating $6,000,000.

Another important metallurgical result was an improved contact metal used in the millions of relays and tiny switches required in telephone plants and central stations. Since 1916 this new metal has earned through savings about $13,000,000.

Another illustration of the earning power of research taken from the experience of the Bell system is the use of so-called phantom circuits. A simple circuit consists of two line wires. In phantoming it is possible to superimpose a third circuit upon two pairs of such wires, utilizing each pair as if it were a single line wire. At present there are about 400,000 miles of phantom circuit in the Bell system. The cost involved in obtaining these phantom circuits was about $9,000,000, but the cost of the additional copper wire necessary to string simple circuits to do this work would have been $90,000,000.

These earnings are real and the income upon the investment in research which makes them possible is greater than that usually obtained in commercial ventures.

Minimizing Human Error

THOSE who have been for long associated with the scientific apparatus and supply business know how continually Americans have been told that it would be impossible, for three principal reasons, to produce precise ware in this country. These reasons are fundamental characteristics which differentiate American business methods from those of most other countries, and upon two of these the success of many an American enterprise has to a large extent depended. First, our standards of living make high wages necessary in practically every line of our activity. Second, to compete successfully with this unavoidable high cost, we have developed automatic or semi-automatic machinery to an unusually high degree. Third, the manufacture of precise scientific instruments requires a patience and diligence, not to say an actual love of one's work, which unfortunately has never been characteristic of the American worker. But those who assured us that precision glassware, for example, would never be made in America, did not take into account American genius in providing mechanical devices which would be almost human in their movements, and which would not only minimize errors of the workman, but provide a substitute for an extreme accuracy which they thought impossible in America.

We are accustomed to think of "shoes and ships and sealing wax," automobiles, typewriters, sewing machines, etc., as standardized and produced in immense quantities, but it has taken Americans to standardize and produce in quantity such an article as an analytical buret of precision. A recent visit to a plant in Vineland, N. J., impressed us most of all with the great genius displayed in minimizing human errors and in attaining a quantity production of precise apparatus which makes it more nearly possible to compete with low wage standards of other countries and to surpass in quality apparatus formerly made solely by hand.

We used to marvel at the skill of the glass-blower who was able to produce standard lengths of tubing, fairly uniform in diameter and thickness of wall, but here is a mechanical device which works continuously and draws tubing to a given size varying not more than 0.2 mm. in diameter and 0.02 mm. in thickness of wall, without striae or air bubbles. Such tubing is blown by the mile and is cut in specified lengths by an automatic machine as it cools.

To be sure, the graduation of a buret made from such an ideal piece of straight tubing is comparatively simple, and yet to do this mechanically, making allowances for slight but inevitable variations, even in machine-made tubing, is an accomplishment worthy of note. The tubing is first fitted with a stopcock and is then coated with wax upon which the engraving is done prior to etching. Bench marks are placed at intervals on the basis of weighed mercury fillings. This part of the process is carried out by an expert operative, using all possible mechanical aids. The tube is next put into the automatic grading machine upon which adjustments are made so that the major divisions coincide accurately with those previously determined. Each interval is automatically graduated with the same number of divisions, and in this fashion error is practically eliminated. The etching of the glass and the removal of the wax, followed by filling the etched marks with color, is but a detail.

The marked success with which ware made in this fashion meets the requirements of the Bureau of Standards is ample evidence of the success of the process. It has taken much expenditure of patience, energy, and capital to achieve what now appears simple. It shows the determination of some Americans never again to be dependent for essentials upon other sources, and if we are so constituted as a people that we compete with difficulty where the work is tedious and oftentimes uninteresting, we appear to have the ability to create machines which will do such labor for us. It is a piece of work undertaken in a field where the monetary returns are not large and the volume of business is never great, but it indicates a spirit which we appreciate and applaud.

Where Lies the Difficulty?

WE HAVE received several comments upon a "want ad" by a member of the SOCIETY which appeared in a recent number of the News Edition.

The following is taken from one of these letters:

> What is wrong with our profession when its younger members insist upon advertising themselves for work "salary unimportant," etc.? (I won't go through the list.) Are we not the doctors of the material world? Has not every trouble in the material world a chemical foundation? Why, then, are the chemists the poorest paid, the worst treated, the most ignored of professional men? Do we act like professional men?
>
> Does the college professor's influence rob the profession of the wage demands its members should make? Does the smallness of the college professor's salary cause him to advise his students to accept niggardly terms? Or, are the graduates and chemists of no greater value than the salary they now earn? Are there too many chemists or too many so-called "chemists?" Does the individual chemist dispense his knowledge too readily to the laymen with the desire to appear learned, forgetting that he is robbing his brother chemists of their wage? * * *
>
> Has professional dignity and disdain for monetary matters dragged the profession down? Probably there are many men who work for science's sake alone, without any thought of using their knowledge as a means to a livelihood, but the great advances in technical work have been made by men whose bread, butter, and position depended upon their getting results.
>
> I know you cannot answer these questions, nor do I expect you to do so. Most of them may be far-fetched. However, I feel that a real problem exists and that something should be done to solve it. We who are in responsible positions should shoulder some of the problems of the under dog, because we are no doubt in some sense responsible for his state of being. It is not an impossible task. The physicians have a dignified profession and yet they charge for it, their elevation in the laymen's mind increasing with their increase in rates.
>
> Why, then, must chemists advertise themselves as willing to work for nothing or almost nothing? Are our graduates so narrowly trained that they can do only one kind of work? Are they single-tracked? Are they afraid of work? Have they been disillusioned? At any rate, after a chemist (a real chemist) has served an apprenticeship of some years, should not his average salary compare favorably with that of men in other professions? How are we going to get rid of the ne'er do wells?

As our friend states, we cannot attempt to answer all these questions. Graduation signifies, not the completion of one's education, but its commencement. The college course is a success if it equips a man so that he can grasp facts readily, know sources of reliable information, and segregate truth from the mass of material offered to him. Because he can do these things the graduate chemist is worth a fair wage and only a fair wage until he begins to become acquainted with the detailed work of his employer. No doubt the employer feels that the experience gained by the chemist should be reckoned as a part of his remuneration; but in too many cases the chemist is kept too long on probation. He should be promoted in a substantial manner, given to understand that such promotion has not been earned, or replaced within a reasonable time. Nothing is so deadening as uncertainty.

The Priestley Medal

THE award of the Priestley Medal to Ira Remsen is another evidence of the work originally undertaken through the enthusiasm of the late Francis C. Phillips. The Priestley Medal is an important award. It is a distinct honor which will be conferred once in three years in accordance with the rules established by the Priestley Medal Committee. This committee has done valuable work in assembling letters, apparatus, and books of Joseph Priestley, and placing much of this material in the old home at Northumberland, Pa., which is being restored as a result of the committee's further activity. There is also the portrait of Priestley presented to the National Museum in Washington, and now this gold medal which will be more and more highly prized as its import is understood. We congratulate Dr. Remsen, who is the first recipient of the medal, and believe its triennial award will be a further incentive to chemists to put forth their best efforts.

MILWAUKEE MEETING

THE events of the short five days occupied by the Sixty-sixth Meeting of the AMERICAN CHEMICAL SOCIETY held at Milwaukee, Wis., September 10 to 14, inclusive, can be recorded in comparatively little space, but only time can record the far-reaching effect which the developments at Milwaukee will have upon the future of American chemistry.

In summarizing, briefly, the outstanding features of the meeting, first place must be given to the two prize awards which will be sponsored by the AMERICAN CHEMICAL SOCIETY as a result of the generous gifts of the Allied Chemical and Dye Corporation on the one hand and Mr. and Mrs. Francis P. Garvan on the other. Stimulation for both the workers in chemistry and those who are about to begin a career is provided through these two magnificent prize offers.

Next in order of importance perhaps was the splendid scientific showing made by the SOCIETY through the work of its divisions and sections, which provided a total of more than three hundred papers on a wide range of chemical and allied subjects. Not only were these papers of intense interest to the assembled members, but many of them furnished interesting newspaper stories, thus keeping the work of the SOCIETY before the public.

The great interest displayed by college men, as well as those identified with the industries, in the subject of chemical education and the general recognition that the future of chemistry depends largely upon the training of the coming chemist, as well as the desire of all to make this training as effective as possible, might well be characterized as another outstanding feature of the meeting.

The award of the first Priestley Medal to Dr. Ira Remsen; the public meeting at which Mrs. Thomas G. Winter, president of the General Federation of Women's Clubs, delivered an address full of practical suggestions for bringing chemistry home to the public; the trip to Madison, Wis.; and lastly, the splendid manner in which the convention was handled by the local committee completes the brief survey of outstanding features, but by no means describes the various other items of business and scientific interest which transpired. Entertainments for all and especially for the ladies were provided most lavishly by the local hosts.

Following the council meeting on Monday, the meeting was formally opened Tuesday morning in Plankinton Hall of the Municipal Auditorium. Clare H. Hall, the chairman of the local section, presided. Welcoming addresses were made by Mayor Daniel W. Hoan, State Senator Oscar Morris, and President Albert C. Fox of Marquette University. President Franklin responded for the SOCIETY, after which two general addresses were delivered. Charles F. Burgess, director of the C. F. Burgess Laboratories, spoke on "Marketing Chemical Discoveries," and Dean Arthur I. Kendall, of the Medical School of Northwestern University, spoke on "Bacteria and the Chemist."

Special general divisional programs arranged by the Divisions of Physical and Inorganic Chemistry, Organic Chemistry, and the Section on Chemical Education occupied the afternoon of the first general meeting day. In the evening a dinner and entertainment were provided which turned the thoughts of those present from science to sociability, and a very enjoyable evening was spent.

All the divisions and sections met some time Wednesday or Thursday, and some on both days. Symposia on "Bread," "Soils, Fertilizers, and Crops," "Synthetic Methods," "Gelatin," "Chemistry of Glandular Products," "Activated Sludge," and "Biological Chemistry" were held in connection with several of the divisional meetings.

The Section on Chemical Education held a joint meeting with the Division of Industrial and Engineering Chemistry and the Milwaukee Chamber of Commerce. While few of the last group attended the meeting, the main object was accomplished, because educators and industrialists were provided with an opportunity to air their views, which they did, and a wholesome coöperative effort will very likely result.

Mention has already been made of two features of the public meeting on Wednesday evening. The closing number on the program of the meeting was an address by President E. C. Franklin on "Systems of Acids, Bases, and Salts."

The trip to Madison, Wis., including inspection of the University of Wisconsin buildings and the Forest Products Laboratory, proved to be very delightful to the one hundred and fifty or more who spent Friday as the guests of the Wisconsin Section. Industrial excursions in Milwaukee had been provided for those not desiring to make the trip to Madison.

Newspapers of Milwaukee were quite generous with their space in recording the doings of the SOCIETY and it was quite evident from this and from the remarks of Mayor Hoan that chemistry has found an important place in the activities of the City of Milwaukee. Doubtless the recent meeting will help to impress its importance more firmly upon the public. This should be compensation, in a small way at least, for the splendid hospitality and untiring efforts of the Milwaukee Section in making the Sixty-sixth Meeting of the SOCIETY so successful.

University Photographic Laboratory

GUESTS OF WISCONSIN SECTION AT MADISON, WIS

The Council Meeting

Past Presidents Bancroft, Herty, Hillebrand, Smith, and Whitney, the officers of the SOCIETY, and 108 councilors were present at the council meeting which was held in Milwaukee on September 10.

The Prize Essay Contest was announced in some detail by the chairman of the committee, whose report was received with the enthusiasm due an undertaking of this importance.

Edgar F. Smith, chairman of the committee appointed after the Pittsburgh meeting to arrange all matters relative to the annual prize made possible by the Allied Chemical and Dye Corporation, reported that the committee had agreed upon "The American Chemical Prize" as the name of this annual award, and that the jury of award is to be a self-perpetuating body consisting of five representing the AMERICAN CHEMICAL SOCIETY and two appointed by the Allied Chemical and Dye Corporation. The Council not only approved the report as presented, but empowered its committee, consisting of Edgar F. Smith, C. F. Chandler, F. P. Venable, Ira Remsen, and Theodore W. Richards, to designate five who are officially to represent the SOCIETY upon the jury of award.

The application of the Section on Chemical Education to become a division was approved. A number of additional fellowships have been founded since our last annual meeting, and Secretary Parsons read a list of existing fellowships including these additions. This list will appear in the Proceedings.

Upon the motion of the Committee on the Metric System it was voted that hereafter the metric system should be used in all SOCIETY journal articles, with English equivalents in parenthesis if the authors so desire. The recent announcement that, following overtures by the drug manufacturers, the Public Health Service and later the Army had abandoned its former policy of purchasing drug and medical supplies by metric units on the plea of a slight economy, brought forth a resolution unanimously passed disapproving this action and expressing great disappointment at the step, which certainly appears to be a backward one.

The report of the editor of the *Technologic Monographs* was approved, as was the interim report of the Finance Committee, presented by the treasurer.

The invitation of the Washington Section to hold the spring meeting of 1924 in that city in April, with definite date to be announced later, was approved. The invitation of the Cornell Section to entertain the annual meeting in 1924 was unanimously accepted.

The Advisory Committee, having given careful consideration to the financial needs of the local sections, brought in a recommendation that beginning with 1924 local sections be given a rebate of \$5.00 on each new member paying \$15.00 dues, and \$2.50 on any nonmember reinstated in membership after an interval of two years, provided this membership is originally transmitted to Secretary Parsons and rebate claimed by the secretary of the local section or the chairman of its membership committee.

It was voted that the Committee on Chemical Education of the Division of Chemical Education be made a committee of the Council.

When the Committee on Progress in Society Procedure reported at New Haven, its recommendation for the establishment of two special committees, one to investigate the question of intersectional or regional meetings and the other the classification of membership, was adopted. Both questions are complicated by a number of factors, and while the Council sees the wisdom of proceeding very slowly, there was some disappointment that circumstances made it impossible for more than progress reports to be made. One of the conditions has been the failure of many local sections to express their views on these questions. Both committees were continued and will endeavor to make reports at the Washington meeting, but no progress can be made by them unless those individuals and groups which have given thought to these matters express their views to the chairmen of the respective committees.

Both these committees having sprung from work before the Committee on Progress in Society Procedure, it occurred to several individual councilors that much time might have been gained had some member of the older committee been placed upon each of these new committees, so that some continuity in the work might have been maintained and the duplication of certain effort thereby avoided.

A new local section, with headquarters at State College, Pa., was authorized as soon as certain formal requirements have been met. The report of the Supervisory Committee on Standard Methods of Analysis was referred to the Advisory Committee and the motion to permit student members to become enrolled in September with dues of \$3.50 for the balance of the year was approved. The editors were reëlected.

Another recommendation of the Council at New Haven creating an Executive Committee to replace the present Committee on National Policy, to have the usual powers of an executive committee and to have full authority to act ad interim for and in behalf of the Council on questions of national policy or import and to serve in an advisory capacity to the Council, was approved. This committee will consist of the immediate past president, the president, the secretary, the treasurer, the editors of the SOCIETY's journals, and three councilors. The present councilors, A. M. Comey and Wm. McPherson, were continued upon the new committee, and George D. Rosengarten was elected as a third member. The provision for the election of directors by some regional plan has been greatly desired by some sections, and a satisfactory plan having been devised by the Advisory Committee, this was unanimously adopted. It will require another year to put the plan into full effect. Full details will be given in the Proceedings.

The size of the Council then came under discussion and the recommendation of the Advisory Committee that the right to substitution be discontinued was refused. A number of other plans were suggested and debated at length, but the final action of the Council was that the size of the body is not to change. This is a reversal of the vote at New Haven.

The name of the Division of Leather Chemistry was changed to Leather and Gelatin Chemistry. There was prolonged discussion of two motions presented by the Leather Division. The first motion was intended to rescind the Council action that no papers be presented unless the titles are printed upon the final program. This motion was lost. The second motion was to bring about a modification of the action taken at Pittsburgh to the effect that nonmembers may not present papers before divisions and sections unless of unusual importance, and then only upon an agreement between the secretary of the division or section and of the SOCIETY. After prolonged debate the Council approved the action of the Secretary so far taken and instructed him to continue his present policy and interpretation, except as provided in an amendment to the Pittsburgh action—namely, "except papers invited by chairmen and secretaries of divisions, and that such papers are to be so designated on the program."

The Council approved the plan of encouraging the Cincinnati Section to organize an intersectional or regional meeting to be held in conjunction with that of Section C at the December, 1923, meeting of the American Society for the Advancement of Science.

While the discussion at times was spirited, the Council was harmonious to a degree. The actions taken were either unanimous or by considerable majorities, and there was both time and opportunity for extensive discussion and the relation of many experiences. After a hearty vote of thanks to all local officers and others contributing to an unusually successful meeting, adjournment was taken at 10:30 P.M.

The Market for Chemical Ideas[1]

By C. F. Burgess

C. F. Burgess Laboratories, Madison, Wis.

Were I to fall into the spirit of the times and try to emulate the big talkers of the day, I would dwell upon the noble work which chemists are doing in the cause of humanity; I would tell how they are being deprived by the big interests of their birthright—a living wage; I would show that they have no real market for their product, that Wall Street controls the situation; and I would urge that it is time for chemists to arise and throw off the shackles which are holding them in the ranks of the oppressed.

But for various reasons, one of which is the scarcity of facts upon which to base such talk, I shall take an opposite course and even at the risk of incurring possible displeasure, I shall refer to the product of the chemists' brains, chemical ideas, as a commodity, and, therefore, subject to barter and exchange. I may find it necessary to depart from the time-honored custom of scientists and refer to the value of chemical ideas in terms of money, and I hope to be able to show that the chemist has in his own control the methods of regulating the returns for his services.

C. F. Burgess

In using the term "chemist" in this discussion, I intend to refer only to those men of chemical training who have ability to do creative work, to produce "chemical ideas," as differentiating from the chemist who is confined to pure routine work, and is like the Ford type of mechanic, whose principal experience is "screwing in bolt No. 647." By the expression "chemical ideas" I refer to the discoveries, inventions, or proposals which are capable of being turned to the service of man through offering a new product, a new process, a "method of making two blades of grass grow where one grew before"—or, in other words, to those ideas which have a value, either immediate or potential.

During the past few years a great deal has been said about the earning power of research. Popular interest has been created. Graduate and undergraduate courses in chemistry show increased enrolment. There is a rapidly increasing volume of chemical literature and the production of chemical ideas is a growing industry. In chemical circles, however, the opinion prevails that the chemist is not sharing adequately in the profits which arise through the application of his ideas. Seldom is the suggestion made that there may be an over-production from chemical research and that the meager returns to the chemist are but a working out of the economic law of supply and demand.

In the sense that there is an established market for manufactured goods, for agricultural and mineral products, for the works of the writer and composer, it might be said that there is no organized or established market for chemical ideas. The producer of chemical ideas must do the best he can in a market which may at best be described as chaotic.

Such market as does exist may be classified into various divisions.

The one which furnishes the easiest path for marketing chemical ideas is that afforded by our scientific and technical societies, and by the publishers of scientific journals. To this the chemist brings his wares in the form of papers, monographs, or theses. There seems to be little restriction upon the volume which can be absorbed. The compensation secured through this outlet is indefinite and comes in a roundabout way. Through a peculiar system which has been evolved in our educational and other publicly endowed chemical laboratories, an investigator's advancement, title, and salary are determined in large measure by his research ability. And this in turn is often measured by the number of papers he has published. The public, which supports these laboratories, is in the end the actual purchaser of these papers, and buys at low prices. Knowing something of the salaries of college research men, and of the amounts which constitute an increase of salary, I would not estimate the selling price to be more than a few hundred dollars per paper.

This market has the advantage of size, and the disadvantage of offering small returns to the producer. It can be criticized from the standpoint of the public. Some weeks ago I participated in a discussion at a meeting of the directors of a national scientific society, the debated question being the increasing mediocrity in the quality of chemical papers finding their way into the chemical journals. The opinion prevailed that the system of forcing laboratory workers to write numerous papers, often presenting fragmentary investigations coupled with a lack of proper censorship as to quality, is a factor contributing to an unfortunate deterioration in current chemical literature. In other words, this market is likely to be disrupted unless attention is given to improving the quality of goods dumped upon it.

The second division of the market for chemical ideas is that in which the chemist contracts to furnish his entire supply to his employer, usually one engaged in the business of manufacturing. The market price is embodied in the salary under which the chemist accepts employment. Many a worker finds this is an unsatisfactory market in which to deal, because it involves sacrifice of independence and an exclusion of other outlets for his discoveries. He feels that this loss is not compensated fully by the amount of salary paid. He may see his ideas adopted freely by the management. Presumably, the corporation prospers, but without giving the chemist the compensation which he considers his due.

When the chemist looks for larger financial return than is afforded through publication, and is unwilling to sacrifice his independence by accepting a salary, he has recourse to a third division of markets, which is open to him if he can show property rights or title to his discovery or invention. This he can do by establishing it as a trade secret, or making it the subject of a United States patent. It is beyond the scope of this paper to discuss trade secrets or patents, but it is certainly not outside the essential duties of the chemist to familiarize himself with the law relating to trade secrets, and the complex details of the patent art, if he ventures into this field of marketing.

Perhaps the chemist who presents his ideas to an unappreciative world may profit by the words of the noted divine who said:

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[1] Title on program, "Marketing Chemical Discoveries."

"When I find an audience cold and unresponsive, I do not seek consolation in blaming the audience. I know there is something lacking in myself and I seek to remedy my defects."

Let us, therefore, look at the position of the chemist from the viewpoint of the public and through the eyes of the business executive who has to deal with research as an adjunct to industry.

From this viewpoint there is no tendency to belittle the importance of chemical research; the fundamental value of chemical ideas is recognized universally; in the distance can be seen new industrial worlds to be conquered through the chemist's leadership. The store house of chemical knowledge to which he is continually adding has become an immensely valuable asset to industry.

But attention must be called to the fact that just as a manufacturer's inventory of raw material may be larger than is necessary for the current needs of a business and thus become a dead rather than a live asset, so the store house of chemical knowledge can be overcrowded with ideas at a rate greater than that at which they can be put to practical use.

This is a condition which must be recognized. It has been estimated that if all chemical research work were discontinued for twenty years, industry would still progress through reduction to practice of the many chemical ideas which have been offered in the past. The lapse of time, sometimes short but usually long, between the chemical discovery and its reduction to commercial practice accounts in part for our large inventory of chemical knowledge, and for the manufacturer's inability to pay large prices for new ideas which cannot be used at once.

To apply an idea may upset a long-established routine carried out by trained workers, involving the upbuilding of a new organization; the discovery of a new and better raw material may mean the abandonment of a plant in one place and its reëstablishment elsewhere; another proposal may have to await the whims of a legislature. Delays such as these may tax the patience of the chemist.

The business man has been criticized for his lack of chemical knowledge, and his consequent indifference to or ignorance of the work the chemist is doing. But it is asking the impossible to expect the busy executive to review and pass judgment on the value of chemical ideas as rapidly as they are presented. In every plant where chemists are employed new ideas and proposals are coming up continually. As a fair index to the number of chemical ideas being offered to the public, the abstracts of the AMERICAN CHEMICAL SOCIETY may be cited. Assuming that each abstract refers to an idea embodied in some book, paper, pamphlet, or patent, the current monthly volumes show that a new chemical idea is presented to the public at the rate of one for every five minutes of the business day.

The immensity of the volume of chemical literature through which the business man struggles in his endeavor to keep abreast of chemical knowledge is bad enough, but the task is made more difficult by the chemist's language, a language of words, formulas, and symbols which mean no more to the uninitiated than the cryptic, mystical expressions of the medieval alchemist do to the modern worker. The truth of this statement can be tested by choosing almost any paper presented before this SOCIETY, and asking some intelligent banker or other type of business man—possessing an academic degree, if you wish—to read the paper and tell what he finds in it. The chances are that he will laugh.

To the complaint that business is blind to the opportunities for profit which the adoption of new chemical ideas affords, the reply is that if the chemist has something meritorious to sell it is necessary for him to practice "the science of human service" (business), which embraces the art of imparting knowledge to the public (advertising).

It is a notorious fact that chemists are deficient in the science of salesmanship; their writings fail by far from "touching the imagination of crowds." I have asked various investigators why they confine their announcements of discoveries to the scientific journals and do not reveal them to the larger public through the daily press. Their attitude may be typified by the following questions and answers of a conversation held some months ago with an active and honored member of this SOCIETY.

If you are disappointed in the interest shown in your recent discoveries, why do you not try an announcement through the Associated Press?

That is out of the question. My principal concern is to see that the daily papers do *not* attempt to describe my work. I have been terribly embarrassed by the garbled reports which have been given out concerning some of my discoveries.

Why do you not prepare, then, an accurate statement in newspaper style? If the subject matter is of importance and written clearly so as to be understandable, your contributions will be welcomed

You are suggesting the impossible, for an adequate description cannot be written without using scientific terms and formulas, which are, of course, unintelligible to the newspaper reader.

That man failed to appreciate the well-known truth that no man can become complete master of his subject without being able to explain it in a manner intelligible to the average man.

The exceptional view was held by another member of this SOCIETY. He has contributed many papers, and could tell you, if he would, that a public press announcement of a certain discovery brought him a hundredfold greater correspondence with interested persons than he had ever had from a paper published in the chemical journals. In other words, as an advertising medium the daily press has a far greater drawing power than has the scientific journal.

While the average chemist finds it impossible to write his own advertisement, there are notable examples of ability in this field. Dr. Robert Kennedy Duncan has shown how the chemical idea can be sold to the public, and although he incurred the displeasure of fellow chemists in his use of popular language, he rendered a monumental service to the downtrodden chemist.

If the popular appeal does not fit in with his standards of ethics and professional pride, the chemist must admit that Pasteur lost nothing in dignity or professional standing when he uttered that forceful appeal which might well be placed among the classics in advertising:

> I have a head full of the most beautiful projects for work. I am ready for new productions. Oh, why am I not rich—a millionaire? I would say to you: Come, we shall transform the world by our discoveries.

The business executive will admit that the salaries of chemical workers are low and that few chemists advance into the better paid administrative and executive positions. But he will deny that there is any system working against the chemist's advancement other than the chemist's own inability or lack of interest in handling the business problems that are always involved in the reduction to practice of a chemical idea.

One employer says that his greatest difficulty with his chemical workers is their tendency to study their equities in the business without showing a willingness to follow the chemical idea from the laboratory through the semicommercial stage and into full commercial operation, or dealing helpfully with all the problems of equipment design, handling of labor, marketing difficulties, and the like.

It is the experience of employers that it takes time for the chemistry graduate to go through the disillusionment period before he can become a valuable coöperating force in the business organization; the longer he has been trained in academic work the harder it is for him to become adjusted to industrial conditions. During a discussion of this feature before a branch meeting of this SOCIETY, the executive officer of one of the largest industrial laboratories said that his company had compiled a rating of the universities on the basis of time taken for graduates to adapt themselves to industrial research and development. Under this rating the range is from four years for some of the larger universities to one year for certain of the smaller. This is mentioned as being suggestive of the help which the educational institutions might give in increasing the service value of their graduates.

From the management standpoint much study has been given the question of adequate compensation to the chemical worker, just as it has been given to other classes of producers; but the chemical idea is such an intangible commodity that its valuation is exceedingly difficult. As an illustration I recall the solution of a problem for increasing the production of a certain manufactured article.

The standard rate of production was 800 per day per employee. The chemist proposed a quick drying adhesive as a means of increased yield, and he showed how the output figure could be increased to 1200. One of the shop workers then made a time study of the operator's movements, redesigned the work tables, and installed a conveyor system, resulting in an increase to 2000, and the shop superintendent, by installing a carefully worked-out piece rate and bonus system, succeeded in increasing the production to about 5000 units per day. It required over a year to effect these improvements and of this time the chemist contributed perhaps two or three days in the beginning of the period.

To value the equities in the final result becomes much like crediting to the little acorn its property right in the tall oak. If the chemist had exercised the opportunity presented to him he could have supplemented his chemical study with suggestions as to management and payment of labor. His contribution to the business success would have been more easy of calculation, and his opportunity for advancement into increased responsibility would have been bettered.

The average chemist is so little posted on patent matters that he shares the general popular misconception of the actual value of a patent. Even though a patent may be secured with little more expense than is involved in the purchase of a good suit of clothes, the newspapers in the home town have a practice of announcing as of news interest the awarding of a patent to one of its local inventors, and as the inventor passes down Main Street he is stopped by his fellow citizens, who congratulate him upon his good fortune.

When he offers his patent to the business executive he is greeted in a far different manner. He is asked whether the patent has been validated by the courts. The cautious investor knows that if a patent happens to be of little value its validity will never be questioned, but that if it is of importance infringement is sure to follow. If the infringers are to be prosecuted, litigation with its attendant expense results. This may necessitate an investment of a few thousand dollars, or a few hundred thousand dollars. Another question raised by the purchaser is this: Will the patent give the right of use without infringing the rights of others? This question is answered in the form of an opinion by the legal department which must first institute a search through all the patent literature as well as other publications. Such a search usually involves an investment of over one thousand dollars, and I have known of validity searches costing over fifty times that figure.

If the inventor is willing to share the labor and expense of conducting these investigations and litigations and coöperate in working out the ideas to a commercial success, he becomes a business man and as such can deal on much better terms in securing his rewards than he can if he wishes to turn over his patented invention without assuming responsibilities.

We may wonder why the chemist holds himself aloof from business affairs. Perhaps his pride and dignity stand in his way. In a suggested code of ethics for chemists, published recently, appears this clause:

> The chemist should not use his professional standing as a means of sponsoring or promoting commercial or other undertakings of a speculative character.

From the numerous hazards surrounding a manufacturing undertaking we know that it cannot help but be speculative in character. Even the railroad business has become so speculative that few will invest in its stock. If the chemist puts himself on a pedestal and refuses his whole-hearted support to an enterprise in which he may believe but which is nevertheless speculative, he places himself outside of a coöperative relationship with the man of business.

In a bitter tirade against existing conditions, entitled "Is a Commercial War between Chemists and Business Men Coming?,"[2] the threat is made that if the interests do not better recognize the chemist's work, there will be an uprising in which chemists will become business men and as such will receive the rewards to which they are entitled. Far from throwing fear into the commercial world the carrying out of this threat would be welcomed by employers who complain that chemists take too little interest in business affairs.

Perhaps a useful step in this direction is being taken by some of our universities in combining business courses with courses in chemistry; but the greatest opportunity lies in encouraging research men who have already received their degrees to take a greater interest and share in working out business problems. Just how this can be done remains for the individual worker to decide.

To the man trained in academic research who contemplates the establishment of a business enterprise, a word and, in fact, several words of caution may be offered. He will find the various state legislatures pass 26,000 or more laws every two years and that many of these involve compliance on his part. He will find that the laxity in ventilating facilities, appliances for safety, and methods of fire prevention found in university laboratories is not permitted in industrial plants. Inspectors of various kinds clothed with governmental authority will call upon him at frequent intervals to tell him just what he must and must not do. Commercial credit houses will ask him to furnish a detailed financial report and proofs that he is willing and able to pay his debts. No matter what his own confidence may be in the success of his undertaking, his banker will tell him that he considers him a purely speculative risk and must continue to do so until he has established a seasoned industry with demonstrated ability to pay dividends over a period of years.

The opportunities for getting into litigation are boundless, and legal expenses become an unavoidable part of his overhead expense. The blue sky department may try to prove he is less prosperous than he thinks he is and the income tax auditors may assert that he is more prosperous than he claims to be. If incidents such as these can be met by the chemist as patiently and cheerfully as he meets the problems involved in laboratory research, the chances for pleasure and profit from his business are excellent.

As bearing upon the opportunities for success in carrying on research as a business venture, I am privileged to describe an experiment which was begun thirteen years ago and is still under way. A small group of men trained in chemical research joined in the organization of a corporation under the laws of the State of Wisconsin, with the purpose of carrying on investigations of the kind which abound in college laboratories. The resulting discoveries were to be marketed as patent rights, trade secrets, as a part of consulting service, or as a manufactured product in which the results of research were to be incorporated.

One of the incorporators had served fifteen years in educational work and in laboratory research along chemical and electrochemical lines. One had ten years' record of both university and industrial laboratory work in chemistry and chemical engineering; another had served for eight years as chemist in an industrial laboratory; another presented ten years' experience in commercial foundry practice and two years in college research. A fifth man had just completed his university training. A practicing attorney constituted the sixth member of the group that conducted the business during the early years.

The thirteen years' record of this organization is an interesting story, ludicrous in some spots, and bordering on the tragic in others. Many chemical ideas were evolved, and all the ways of marketing hitherto referred to were tried out. Many of the undertakings failed, and some of them succeeded. Licenses have been granted on some of the ideas, other ideas have been sold, still others have been made the basis of manufacturing business controlled by the laboratory corporation.

Whether the experiment as a whole is a success may be a matter of opinion. To form the basis of such opinion I may give some facts. The original capital was $9000. This has been increased through earnings and sale of stock to over $900,000. The annual sales of ideas and of material products have increased to $3,000,000, and with a world-wide distribution. Manufactured products of others and employing the discoveries of the laboratories run into much larger figures. Two industries manufacturing new products have been created and several other similar projects are now under way. The personnel has naturally increased greatly in numbers to a total of over six hundred men and women. At the present time twelve of these are men trained in science and engineering, most of whom occupy executive positions or are actively engaged in directing productive work.

What about the rewards which come to the individual workers? As to how their financial returns compare with those received in other fields, I am unable to say, but there is abundant evidence to show that inspiration and joy come in prosecuting research under conditions in which the worker can watch his idea, started in the laboratory, becoming an instrument of service to mankind.

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[1] *Chem. Age*, **31**, 255 (1923).

[2] This Journal, **14**, 356 (1922).

Bacteria and the Chemist

By Arthur Isaac Kendall

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IT IS distinctive of the fundamental sciences that as their respective fields of inquiry become more completely explored, frontiers which in earlier periods of their development appeared to limit their scope, imperceptibly merge with those of related or coextensive subjects. This tendency toward amplification is peculiarly noticeable in the history of chemistry. In the earlier days, before complex compounds of carbon were well studied, the phenomena of life processes and the environmental interchanges associated therewith were presumed to be endowed with an intangible "vital principle," wholly unapproachable from the investigative side. With the rise and development of organic chemistry, however, and particularly after the synthesis of urea—an important waste product inseparably associated with higher animal life—from ammonia and lead cyanate by Wöhler (1828), the vitalistic conception of life began to give way. The belief is rapidly gaining ground that the dynamics of life itself may be expressible in terms of chemical equations; indeed, some of the simpler of these equations are already qualitatively understood. At the present time, of all the fundamental sciences, biological chemistry, "the handmaiden of medicine," is justly regarded as holding forth the greatest promise of fruitful contributions to the interpretation of the mysteries of these vital processes.

A. I. Kendall

Life appears to be essentially a continuous interchange between an organism and its environment. Death intervenes when this interchange ceases. The investigation of the nature of this interchange lies within the domain of chemistry. In organisms of great structural differentiation, as animals and man, the association of many simultaneous reactions, inevitable from the cellular division of labor, masks the elemental phenomena of the chemical interchange which continually takes place between the organism and its environment. It seems justifiable, therefore, to turn to simpler living entities than man or animals for the unfolding of the chemical pattern upon which the more complex reactions are molded.

Among the simplest of known living things are the bacteria, that group of asexual, unicellular organisms found at the very foot of the ladder of life. All the fundamental phenomena and manifestations of life—morphology, hereditary architecture, nutrition, and reproduction—are performed in this group by units so minute that fully fifteen millions of million of them would scarcely balance an ounce weight. The ratio of surface exposure to volume, furthermore, a factor which determines in a very large degree the magnitude of their energy requirements, is relatively great.

Finally, reproduction is, or may be, extremely rapid among the bacteria. In the more vigorously growing types, as for example the cholera microbe, that dread germ which incites Asiatic cholera, successive generations of fully mature organisms may appear at intervals as frequent as every fifteen minutes. In as much as there are ninety-six periods of fifteen minutes' duration in one day, the theoretical descendants of this germ would be 2^{96} in twenty-four hours. This is indeed a truly prodigious number; fortunately, it never is and never can be even approximated. Nature interposes insuperable barriers to such a theoretical progeny, but even with the limitations of diminishing food supply, accumulation of waste products, and other environmental deterrents, the spawn of a single microbe number countless millions within a very short time.

These facts, together with the comparative readiness with which pure cultures may be procured and kept alive, make the bacteria peculiarly adapted to the study of the chemical phenomena of life reduced to its lowest terms. Such studies as have been made of the nature of the chemistry of bacterial interchange with their nutritive environment—their metabolism, as it is properly designated—have revealed an unexpected similarity with the general phenomena of metabolism in higher organisms, as animals and man. Perhaps this might have been anticipated.

Bacteria are fundamentally digestive systems, and they are endowed with the power of deriving the energy essential for their life processes from chemical substances of varied, but by no means unlimited, composition and stereo-configuration. Each kind of microbe, indeed, exhibits striking fastidiousness in its choice of these energy-containing substances. Herein lies a most important relationship between the microbe and the chemist. A word in explanation will make this point clear.

There are two important phases clearly discernible in the life history of bacteria—a structural phase, in which the microbe reproduces and transmits to its progeny the hereditary chemical architecture characteristic of its kind; and an energy phase, in which the mature microbe and its descendants perform their characteristic functions, or chemical transformations of their nutritive environment.

In point of time the structural phase precedes the energy phase. In the amount of chemical interchange, the energy phase exceeds the structural phase many fold. Also—and this is important—the general characters of the chemistry of structural development and that of the energy interchange are quite unlike. The former is inseparably associated with the proteinization of nitrogen; the latter is inextricably bound up with the oxidization of carbon.

Stated differently, nitrogen is as essential for the structure of the bacterial cell as iron is for the structure of a locomotive; and carbon is as necessary for the energy requirements of the bacterial cell as coal is for the moving of the locomotive. The amounts of chemical substance required, respectively, for the structural and energy phases of bacterial development also are very unequal, even as the weights of iron and of coal are unequal in the respective structural and energy phases in the life history of the locomotive.

A suitable medium frequently used for the cultivation of most bacteria is prepared from a clear watery infusion of meat, reinforced with peptone. This is ordinarily referred to as plain nutrient broth, or plain broth. It contains salts, including phosphates, water, and complex compounds of nitrogen, carbon, hydrogen, and oxygen. The latter are complexes of the amino acids, of which about nineteen are well known. These in various combinations confer upon proteins their specificity. In such a medium most bacteria find all the nitrogenous constituents for their structural needs and also the carbon necessary for their energy requirements.

Bacteria could not grow if nitrogen in proper combination were not available; hence, this plain broth, which offers to bacteria the requisite nitrogenous constituents, is the nutritive basis for ordinary microbic cultivation.

The carbon of amino acids and of peptone is not so readily utilized for energy, however, as the carbon of carbohydrates; consequently, it is frequently advantageous to add some glucose or lactose, or other member of the carbohydrate group, to the plain broth. In such a glucose broth or lactose broth medium, the microbes clearly have a choice between the carbon of the amino acids and the carbon of the carbohydrates for their energy requirements. If the stereo-configuration of the protoplasm—that is, the living substance—of the microbe fits the stereo-configuration of the glucose, or the lactose, or whatever carbohydrate has been added, the microbe will turn to the sugar for its energy in preference to the amino acid, utilizing the amino nitrogen of the latter, of course, both for its own structural needs and the structural needs of its progeny. In physiological parlance, the utilizable carbohydrate spares the protein constituents of the medium from bacterial decomposition, aside from the very small amount of the latter required to build up the bodies of the microbes.

It is not a matter of indifference which type of compound, carbohydrate or amino acid, is used by the various microbes for energy. Thus, diphtheria bacilli grown in plain broth, containing no carbohydrate, produce that extremely potent soluble poison or toxin known as diphtheria toxin, which constitutes the aggressive weapon of this formidable germ. If, however, a small amount of glucose is added to plain broth before the diphtheria bacillus develops in it, the resulting growth product is radically different. It no longer contains the potent poison; in place of this powerful toxin the culture medium contains lactic acid, the chemical basis of buttermilk.

Here is in actuality the realization of that strange conception of Dr. Jekyll and Mr. Hyde, which Robert Louis Stevenson has made so well known. The plot is unique. The same individual, under the influence of a chemical, changes his disposition from that of a useful member of society to that of a miscreant. The difference between diphtheria poison and buttermilk is surely as great a divergence in activity as that of the dual personality of the fabulous Dr. Jekyll and Mr. Hyde.

The striking change brought about by the addition of utilizable carbohydrate to a plain broth inoculum of the diphtheria bacillus is but one of a large number of examples well known among the bacteria, however, and its significance is far deeper than a mere actual living instance of a hitherto pleasant myth.

In the field of medicine, for example, the baneful effects of typhoid, cholera, dysentery, and other germs that cause severe infections in the alimentary canal can be ameliorated through proper dietary procedures, and the character of their products can be changed from poisons to lactic acid by the same measures that reformed, as it were, the activities of the diphtheria bacillus in culture media. This procedure of dietary therapy has been practiced successfully in typhoid and dysentery.

For the chemist, however, the underlying principle of the influence of carbohydrates upon the character of microbic chemistry has a very practical bearing. Space does not permit of a discussion of the possibilities in this field except in a relatively restricted group of substances, the carbohydrates. Inasmuch as carbohydrates are of great interest and importance both in animal and human nutrition and in many industries, however, this limitation is not incompatible with a survey of the relations of the microbe to the chemist.

Returning to the diphtheria bacillus, it will be recalled that in a plain, glucose-free medium, a potent specific toxin is produced. Also, the reaction of the medium becomes progressively more alkaline. In the same medium to which glucose is added—that is to say, in glucose broth—there is no toxin formed and the reaction becomes progressively acid, owing to the formation of lactic acid.

Herein lies a chemical test for glucose. Either the absence of toxin or the increase in acidity would with suitable controls be diagnostic. Extending this type of test to a library of microbes, each of which possesses the power of fermenting or utilizing certain definite carbohydrate configurations, there is at once available a new method of detecting and identifying members of the carbohydrate group.

Several methods of procedure follow from this utilization of microbes as chemical reagents. First, the identification of an unknown member of the sugar group. This is readily accomplished through a series of bacteria, each of which will use only certain sugar configurations.

Secondly, the recognition of impurities in carbohydrate samples.

Thirdly, the quantitative estimation of carbohydrates, both singly and in mixture.

Fourthly, the identification of hydrolytic products resulting from the cleavage of complex carbohydrates.

These various procedures have been used successfully in a limited group of sugars, and the entire carbohydrate group is open to exploration by this comparatively simple method of microbic analysis.

It is of some interest to know how sensitive the bacterial reagent is—how small an amount of sugar can be definitely detected. A long series of experiments has shown that as little as one one-thousandth of a per cent, or one one-hundred-thousandth of a gram, of a utilizable carbohydrate dissolved in a cubic centimeter of a culture medium may, under favorable conditions, give definite indication of its presence.

When one realizes that two unlike sugars, as glucose and lactose, may have nearly the same optical rotation and about the same reducing power, it will be seen that the microbe holds forth possibilities of interest and importance in this field.

In the animal and human bodies, several problems are still unsolved which would seem to be approachable from the standpoint of the microbe chemist—the place of formation of lactose in the lactating animal; the differentiation between glucose, pentoses, lactose, and glycuronic acid in the urine; the identification of the sugars which are found in the nucleins and in the brain, and also the stereo-configuration of the sugar in the blood and the tissues.

The direct relationship between glucose, the sugar of the blood and tissues in the human body, and the energy derived therefrom focuses attention upon the corresponding phenomena in bacteria. The stereo-configuration of the protoplasm of the living cell and its ability to utilize a similar, compatible sugar configuration seems to be one of the fundamental reactions of life itself. The intimate workings of this energy complex yet remain to be unfolded, and the answer must be sought for in the domain of chemistry.

Finally, a word about bacteria in the industries. Some of the most venerable processes known to mankind depend upon microbic participation. The retting of flax in the manufacture of linen, the tanning of leather, various fermentation processes associated with the souring of milk, sauerkraut, ensilage, the manufacture of vinegar, and various alcohols, as butyl, and ethyl alcohol, acetone, glycerol, and even the initial steps in the manufacture of synthetic rubber, are but a few instances of the deliberate exploitation or spontaneous activity of microbes.

As time goes on and knowledge becomes more complete, the chemist will utilize this cheap, ceaseless energy of the microbe to perform almost numberless processes that are unattainable at present or accomplished only by an extortionate expenditure of energy.

NINTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

UPON entering the Ninth National Exposition of Chemical Industries held at the Grand Central Palace, New York, September 17 to 22, one's first impression was that the entire scheme of things had been arranged with taste and a keen eye to a general pleasing effect. At the extreme end of the center aisle hung a large placard bearing this legend:

> **CHEMISTRY IS THE PRIMARY ELEMENT THAT GOVERNS SUCCESSFUL MANUFACTURING**
>
> If the chemical and chemical equipment industries represented at the Exposition should cease operating for one year, every vital industry of the United States might be forced to suspend operations before the expiration of that period.—*Rubber Age.*

The most casual visitor could not fail to be impressed with the fact that the chemical industries play an increasingly large part in the world's work. Former expositions were not so well balanced as the one of this year; the individual exhibits showed greater thoughtfulness on the part of exhibitors and concentration upon a few products or pieces of apparatus, which were thereby made more interesting and intelligible to the visitor. Fewer booths contained the conventional lounging chairs and settees, and there was a tendency on the part of all exhibitors to add something of educational value to the exposition and to avoid merely filling their space with miscellaneous collections of unrelated material. As a result more real information was available than on previous occasions; definite ideas definitely presented were met everywhere.

Undoubtedly, the exhibitors are profiting by the experience of previous expositions, and, following the agitation of last year for a different type of exposition under a different management, it appears certain that the management of the National Exposition of Chemical Industries has made an effort to meet some of the criticisms. The enlarged advisory committee, upon which all the elements of the industry are now represented, has had a more deciding voice in the proceedings than heretofore. The results speak for themselves. From year to year the exposition has contained fewer representatives of the actual manufacturers of chemicals and an increasing number of those who have something to sell to the chemical industry. Chemists generally look upon this as undesirable, for, if continued, this policy would result in an exposition of those who are purveyors to chemistry rather than one which demonstrates the progress of chemistry in America. This fault has been overcome to some extent by the equipment of booths to illustrate the progress of special branches of the chemical industry, rather than the products of individual manufacturers.

A notable example of this was the booth devoted to American dyes, where the contention that "American Dyes Are Fast" was clearly demonstrated through the coöperation of manufacturers of dyes and textiles and laundrymen, ably assisted by a manufacturer of dress patterns and attractive living models. The exhibits devoted to insulin and intarvin, the year's outstanding chemical contributions to the treatment of diabetes, to chemistry in the service of radio, to the Chemical Warfare Service, to the Bureau of Standards, and the illustrations of the earning power of research presented by the AMERICAN CHEMICAL SOCIETY, all present new developments in the service of chemistry to civilization and show to what extent exhibits interesting to both the chemist and the public may be made a part of the exposition. The demonstration of such new developments is believed to be more effective than the use of booths to display numbers of specimen bottles filled with materials already familiar to those who visit the exposition.

The experience of certain groups of chemical engineering students in utilizing the opportunities for instruction afforded by the exposition led to the initiation of a new policy at the Ninth Exposition. Before the summer vacation professors were invited to enrol members of their classes, particularly juniors in chemical engineering, in a Students' Course on the Fundamentals of Chemical Engineering and Industrial Chemical Practice. Of those who registered about 125 took the course, which had the following major topics:

1—Plant Equipment in the Chemical Industries
    (*a*) Disintegration—Crushing and Grinding
    (*b*) Mechanical Separation—Grading
        General discussion led by GALEN H. CLEVENGER
    (*c*) Separation of Solids from Liquids—Thickening, Filtration, Centrifugal Separation
        General discussion led by H. N. SPICER
    (*d*) Separation with Phase Change—Evaporation, Distillation, Drying
        General discussion led by W. H. MCADAMS
    (*e*) Handling of Materials
        General discussion led by A. E. MARSHALL
2—Materials of Construction, What Materials to Use: When, Where, and Why
        General discussion led by W. S. CALCOTT
3—Chemicals in Commerce, the Distribution of Chemicals
        General discussion led by E. V. PETERS

Under each of these topics a number of specialists contributed from their experience, and this, together with afternoons and evenings spent in the studies of exhibits and of industrial motion pictures, led up to a general review, various quizzes, and a checking of reports. To facilitate the arrangement of the course Columbia University generously arranged for housing visiting students. The students' course satisfactorily replaced the special addresses heretofore included in the program of the exposition. Each afternoon and evening special programs of motion pictures were offered, these being industrial in character and especially informing.

With this year the plan of the exposition is to be changed to biennial. This should result in an increase in the number of exhibits, the ease with which they are planned, and the interest which they carry when the Tenth Exposition is opened. The chemical manufacturers themselves must not fail in their support of the enterprise, since it is directly in their interest to assist in thus bringing to the public a clearer understanding of what the chemical industry as a whole means to it. The view held by some that the only people exhibitors care to have call at their booths are those in position to leave an order, we believe to be narrow, for, while few of the exhibitors cater directly to the public through retail channels, yet ultimately all the products of the industry are consumed by individuals whose interest should be secured and held. Very few of the questions asked by the visiting public are unintelligent, and the effort made this year to have exhibits clearly understood seems to be an argument against discouraging the attendance of the general public.

The management deserves much credit for the wide publicity given the exposition. The attendance of a large number of business men is due to its efforts. To describe the individual exhibits would require more space than is available here, but if the number of exhibitors was less than last year, there is no doubt but that the interest of the visitor was more securely held than on previous occasions. The chemists are grateful for the support given the enterprise, and the AMERICAN CHEMICAL SOCIETY acknowledges with appreciation those laboratories which contributed examples of their work to prove that research does earn dividends.

All in all the Ninth Exposition showed a marked improvement over the Eighth and may be taken as an indication that the one two years hence will be the best of its kind yet conceived.

American Chemical Society Exhibit

It is the privilege of This Journal to publish from time to time references to the earning power of research, and in line with this policy there were shown at the booth of the Society a few concrete examples of research as a factor in earning dividends. Materials displayed were contributed by the Industrial Fibre Company, the National Lamp Works of the General Electric Company, the Geophysical Laboratory of the Carnegie Institution of Washington, the Union Carbide & Carbon Research Corporation, the General Electric Company, the Ward Baking Company, the Union Pacific System, Arthur D. Little, Inc., and the Miner Laboratories. The materials, arranged in units, were made self-explanatory by large placards, the wording of which is quoted below:

Research in Growing Sugar

Wastes utilized to prevent other wastes is often the result of research. Ten tons more cane per acre (equivalent to one ton raw sugar) and 50 to 70 per cent less labor in the field followed the use of a paper made from waste cane bagasse in the cane fields of Hawaii to prevent the growth of weeds.

Research on Water Supply

The life of locomotive boilers has been lengthened sevenfold and the coal consumed in operation reduced by many millions of tons per year through the application of research to water supply on our railroads. The life of a locomotive fire box (costing $1700) on a certain bad water was two years. After treating the water properly to prevent corrosion, the steel lasted fourteen years, making a saving of more than $700 per locomotive per year.

Research in Bread Making

Two outstanding examples of the value of research to the baking industry:

(1) A food for yeast, consisting of a mixture of mineral salts, prevents a yearly waste in the fermentation process of 200,000 barrels of flour, 30,000 barrels of sugar, and 15,000,000 pounds of yeast. These savings reach the amazing total of $5,000,000 yearly.

(2) A loaf of white bread which contains within itself all the elements necessary for a complete diet. The composition to this bread and the comparative feeding experiments on animals are shown. Experiments on human subjects have not yet been completed.

Research and X-Rays

The modern efficient X-ray tube is distinctly a product of research, and is becoming more and more a tool for further research. Its uses in treating disease, in watching the functions of the vital organs in the human body, and in detecting foreign substances in living and inanimate bodies are well known. The use of X-rays in determining the constitution of matter (space arrangement of atoms in the molecules) is still in its infancy, but results already achieved indicate that future accomplishments in this field will be of extreme importance in the solution of this problem.

Research in Electric Lighting

Organized and continuous research on the lighting problem has produced types of lamps with which this country's lighting bill in 1922 was one and a half billion dollars less than the cost of the same amount of light if the best lamps available less than 20 years ago had been used. This represents a saving, among other things, of 25,000,000 tons of coal.

Research on Waste Material

The value of oat hulls is increased 800 per cent by conversion into furfural, the cheapest commercial aldehyde, having many industrial uses. Thus through research a waste becomes a raw material for a new industry.

Research and Artificial Silk

Through research, wood pulp and other cellulose materials valued at approximately five cents per pound are converted into artificial silk, valued at an average of $2.50 per pound. The value of the artificial silk produced in the United States is approximately forty-five million dollars per year.

This exhibit shows viscose silk made from wood pulp.

Accelerators of Vulcanization

By G. Stafford Whitby

McGill University, Montreal, Canada

HAD it not been that the mixture employed contained a catalyst, Goodyear might not have discovered the peculiar effect of heating rubber with sulfur, now known as vulcanization, which involves such an important change in the physical properties of rubber that it is the basis of the present-day rubber manufacturing industry. The catalyst used by Goodyear was an inorganic lead compound, and inorganic catalysts, particularly oxides of lead, calcium, and magnesium, have been continuously and largely used by the rubber industry, although it is only recently that an explanation of their mode of action[1] has seemed possible.

G. Stafford Whitby

Within the last decade it has been found that many organic compounds act as accelerators of vulcanization, and a number of such compounds have come into wide technical use. Organic accelerators have proved to possess capabilities so much wider and more valuable than those of inorganic accelerators, that they have attracted much more study than has been given to the latter. Furthermore at the time their existence was discovered, rubber manufacturing, which had previously been conducted on almost entirely empirical lines, began to be an object of scientific study.

To designate an agent which when present in a small proportion hastens the rate of vulcanization of rubber, the term "accelerator" is preferred to "catalyst," because it is believed that, in some cases at least, not the agent originally introduced into the rubber, but a product derived from it by decomposition or reaction is the actual catalyst, and because it is not improbable that in some cases the active substance is gradually changed during the course of vulcanization into an inactive product. Few or no investigations, however, have been made to determine the possibility of isolating quantitatively from a vulcanizate an accelerator originally introduced.

The number of compounds capable of accelerating vulcanization is so large, they vary so much in potency and in the character of their effects, and their potency is influenced so much by some components of rubber mixings other than rubber and sulfur, that the field which they present for both scientific and technical investigation is very large. Among the accelerators which are or have been most widely used in technical practice are the following: aniline, hexamethylenetetramine, anhydroacetaldehydeaniline, aldehyde ammonia, and thiocarbanilide. These may be considered as representative of the following three classes of substances in which many accelerators have been found: (1) bases; (2) condensation products of aldehydes with ammonia or amines; (3) thioureas. Most of the accelerators used technically are comparatively mild in their action. The order of their potency may be indicated roughly by saying that 1 per cent will reduce the time of vulcanization to one-half to one-sixth of that required in the absence of an artificial accelerator.

Ultra-Accelerators

Within the past three years or so the attention of investigators has been directed chiefly to classes of substances, the potency of which as vulcanization accelerators is of a much higher order than that just indicated. These more active agents have been distinguished from the milder ones by calling them "ultra-accelerators." Their activity is such that they can produce vulcanization with a proportion of sulfur which would be too small and at a temperature which would be too low for vulcanization in their absence. The term "ultra-accelerator" has been defined by the writer in the sense of this ability.[2] In the future the distinguishing prefix "ultra" may no longer be necessary, for the possibilities which such accelerators present are so valuable that probably they will in the course of time be the main class of accelerators used in practice. Their general employment will demand some modifications in present-day manufacturing operations and a great deal more study before completely satisfactory results can be obtained.

The degree of potency of ultra-accelerators may be illustrated by some data (obtained in conjunction with A. H. Smith) on the dithiocarbamate obtained by the addition of piperidine to carbon disulfide—piperidinium pentamethylenedithiocarbamate ($C_5H_{10}N.CS.SNH_2C_5H_{10}$).

Table I and Figs. 1 and 2 show the effect of one part of the accelerator on the vulcanization of a mixture (rubber, 90; sulfur, 10; zinc oxide, 10 parts) which is vulcanizable without an accelerator.

Table I—Vulcanization of Mixture A

Without Accelerator					With Accelerator				
Time Hours	T_B[a]	L_B[b]	$\frac{T_B \times L_B}{100}$[c]	L_{750}[d]	Time Minutes	T_B[a]	L_B[b]	$\frac{T_B \times L_B}{100}$[c]	L_{750}[d]
Cures at 141° C.									
1	1300	970	12,610	845	1	3440	810	27,864	585
2	1440	940	13,536	808	2	3125	685	21,406	466
3	2200	865	19,030	694	3	355	280	994	...
4	2000	815	16,300	643	5	300	205	615	...
Cures at 131° C.									
1	690	1060	7,314	(1084)	1	2740	850	23,290	659
2	1030	1030	10,609	968	2	3500	750	26,250	535
3	1093	971	10,613	891	3	3450	710	24,495	480
4	1410	930	13,113	813	5	365	290	1,058	...
5	1500	895	13,425	763	.	....	...	....	...

[a] Breaking stress in pounds per square inch.
[b] Percentage length at break.
[c] Tensile product.
[d] Percentage length at a load of 750 pounds per square inch.

At 141° C. (Fig. 1) vulcanization for 1 minute with the accelerator serves to bring the stress-strain curve to a lower position than vulcanization for 4 hours without it, and vulcanization for 3 minutes with the accelerator results in a brittle product—that is, in a complete overcure. It would appear that without the accelerator a cure for about 300 minutes would be required to bring the curve to as low a position as that occupied by the curve obtained by vulcanization for 1 minute with the accelerator. Hence, the acceleration factor for 1 per cent of this accelerator in the mixture in question is about 300° at 141° C. At 131° C. (Fig. 2) vulcanization for 1 minute with the accelerator brings the curve into a lower position than vulcanization for 5 hours without it, and vulcanization for 5 minutes leads to a complete overcure. It would appear that without the accelerator a cure for nearly 7 hours would be necessary to bring the curve into as low a position as that occupied by the curve corresponding to the one obtained by curing for 1 minute with the accelerator.

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[1] Bedford and Winkleman, in a paper presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923; Seidl, *Gummi-Z.*, **25**, 710, 748 (1911); Scott and Bedford, This Journal, **13**, 125 (1921).

[2] *J. Soc. Chem. Ind.*, **42**, 369R (1923).

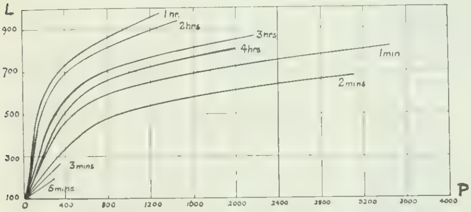

FIG. 1—VULCANIZATIONS AT 141° OF MIXTURE A (1 TO 4 HOURS WITHOUT ACCELERATOR; 1 TO 5 MINUTES WITH ACCELERATOR)

On the basis of the stress-strain curves, then, 1 per cent of the accelerator, in the presence of 10 parts of zinc oxide, increases the speed of vulcanization of a 90:10 rubber–sulfur mixture 300 to 400 times at temperatures from 131° to 141° C.

In Table II the potency of the accelerator is still more evident. This table shows the effect of one part of the accelerator on Mixture B (rubber, 90; sulfur, 2; zinc oxide, 10) which is for all practical purposes unvulcanizable in the absence of the accelerator.

TABLE II—VULCANIZATION OF MIXTURE B WITH ACCELERATOR

Time Minutes	T_B	L_B	$\frac{T_B \times L_B}{100}$	L_{760}
		Cures at 141° C.		
2	505	420	2,121	...
5	305	310	945	...
10	300	320	960	...
		Cures at 131° C.		
2	3630	850	30,855	583
5	3770	760	28,652	505
10	450	375	1,687	...
20	460	390	1,794	...
		Cures at 115° C.		
5	3500	855	29,925	617
10	4300	790	33,970	550
20	3930	740	29,082	485
30	4100	735	30,135	468
60	3180	670	21,306	468

Without the accelerator, heating for periods of 1, 2, 3, and 4 hours gave products which were practically unvulcanized, the highest value for T_B for any one sheet being less than 100 pounds per square inch.

In the absence of the accelerator the material remains practically unvulcanized after heating for 4 hours at 141° C. In its presence the stock is badly overcured by heating for 2 minutes at the same temperature and well cured by heating for 2 minutes at 131° F. or for 5 minutes at 115° F. The tensile strength obtainable in the vulcanized product is greatly increased by the use of the accelerator (Figs. 1 and 2).

Ultra-accelerators increase the speed of vulcanization so greatly that with their aid it becomes possible to vulcanize rubber mixtures at room temperatures. Their practical use for the cold vulcanization of rubber goods is as yet hardly beyond the experimental stage. A great deal of investigation must be conducted on the proportion of sulfur, choice of accelerator, proportion of accelerator, and composition of the mixture before the vulcanization of the various rubber mixtures in a tire, for example, can be satisfactorily and simultaneously conducted in the cold, to give a product possessing all possible improved physical properties and also aging well. But ultimately rubber manufacturers will probably find it possible to dispense with much of the expensive equipment now required for hot vulcanization.

Some evidence indicates that many accelerators improve the aging of vulcanized rubber, especially when the proportion of sulfur and accelerator is rightly balanced.[3] A more intensive study of the nature of aging is desirable. Marzetti[4] concludes that aging is essentially dependent upon the absorption of oxygen by rubber. It should be possible to choose accelerators of such a nature and to use them under such conditions that rubber goods with aging properties greatly superior to those of the products now usually made can be prepared.

One of the difficulties which may attend the practical employment of ultra-accelerators, because of the great activity of these substances, is "scorching," or premature vulcanization, during the mixing and other preliminary operations. This difficulty, however, is not likely to prove insuperable. Various preventative procedures have already been suggested.[5]

REACTIONS OF ULTRA-ACCELERATORS IN VULCANIZATION

The question of the reactions of accelerators during vulcanization raises some interesting points in organic chemistry. As Bedford and Sebrell[6] have remarked, while the reactions of organic compounds with sulfur have hitherto been of interest with respect to the sulfur colors, such reactions now become of interest with respect to the vulcanization of rubber. A study of the behavior of organic compounds, such as those employed as vulcanization accelerators, towards sulfur at temperatures lower than the temperatures used in the production of sulfur dyes is desirable.

Within the two or three years during which the reactions and mode of action of vulcanization accelerators have received attention, very satisfactory progress has been made. A scheme intended to cover a number of cases has been put forward by Bruni and Romani,[7] and a more comprehensive one by Bedford and his co-workers.[8] There are, however, many elements of speculation in both these schemes, which to a large extent must be regarded as merely suggestive of the types of reactions which accelerators probably undergo

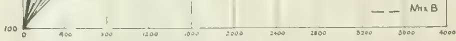

FIG. 2—VULCANIZATIONS AT 131° (1½ TO 5 HOURS WITHOUT ACCELERATOR; OTHER CURES WITH ACCELERATOR)

in vulcanization and as offering working hypotheses on which to base a closer study of the various classes of compounds capable of accelerating vulcanization.

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[3] Schidrowitz and Burnand, *J. Soc. Chem. Ind.*, **40**, 268T (1921); Whitby and Walker, THIS JOURNAL, **13**, 816 (1921); Marzetti, *Giorn. chim. ind. applicata*, **5**, 122 (1923).

[4] *Loc. cit.*

[5] Pestalozza, *India-Rubber J.*, **65**, 623 (1923); Morton, U. S. Patent, 1,434,908 (1922); Romani, *Le Caoutchouc*, **19**, 11626 (1922).

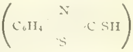
[6] THIS JOURNAL, **13**, 1034 (1921).

[7] Bruni and Romani, *India-Rubber J.*; Romani, *Le Caoutchouc*, **19**, 11626 (1922).

[8] THIS JOURNAL, **15**, 720 (1923).

The most active accelerators known belong to the following classes of compounds:

1—Salts of dithiocarbamic acids from secondary amines ($R_2N.CS.SM$)
2—Dithio acids and their salts ($R.CS.SM$)
3—Xanthates ($RO.CS.SM$)
4—Mercaptobenzothiazoles and their mercaptides



$$\left(C_6H_4\begin{matrix}\diagup N \diagdown\\ \diagdown S \diagup\end{matrix}C.SH\right)$$

5—Disulfides corresponding to the foregoing classes:
  (*a*) Thiuram disulfides ($R_2N.CS.S.S.CS.NR_2$)
  (*b*) Di-dithioacyl disulfides ($R.CS.S.S.CS.R$)
  (*c*) Dixanthogens ($RO.CS.S.S.CS.OR$)
  (*d*) Di-benzothiazole disulfides

Bruni and Romani[7] found that such disulfides are "auto-ultra-accelerators"—that is, they are capable of bringing about the rapid vulcanization of rubber in the absence of free sulfur.[9] These authors assume that this capacity is due to the splitting off of sulfur in an active form, accompanied by the conversion of the disulfide into a monosulfide.[10]

$$X.CS.S.S.CS.X \longrightarrow S + X.CS.S.CS.X$$

They also believe that the accelerating action of accelerators in the first four classes is dependent upon their conversion into the corresponding disulfides. This conversion they regard as being brought about by the action of sulfur on the zinc salt, the latter being the substance originally introduced or being formed from that substance by reaction with zinc oxide. The presence of this oxide is essential in order that all these accelerators may display their full activity.

$$(X.S)_2Zn + S \longrightarrow X.S.S.X + ZnS$$

Certain pieces of evidence tell against the correctness of this view. Bedford and Sebrell[11] find that zinc dimethyldithiocarbamate undergoes little or no reaction with sulfur when heated with it at vulcanization temperature (in boiling xylene). Although from the view stated above, it is reasonable to expect the disulfides to be somewhat more active than the zinc salts, it has been found[12] that the disulfides of Classes 5*a*, 5*b*, and 5*c* are appreciably less active than the corresponding zinc mercaptides of Classes 1, 2, and 3. Maximoff[13] has found that when they are melted with zinc oxide thiuram di- or monosulfides give zinc dithiocarbamates. Bedford and Sebrell[11] find that, whereas zinc dimethyl dithiocarbamate will vulcanize a rubber–sulfur–zinc oxide cement at room temperature, the corresponding thiuram disulfide fails to do so.

Bedford and Sebrell, however, state that in the presence of hydrogen sulfide the disulfide will vulcanize at ordinary temperature, which result they ascribe to the formation of the zinc dithiocarbamate, as follows:

$$X.S.S.X + H_2S \longrightarrow 2X.SH + S$$
$$2X.SH + ZnO \longrightarrow (X.S)_2Zn + H_2O$$

Maximoff[14] and Bedford[11] almost simultaneously expressed the view that in the case of all substances belonging to Classes 1 to 5, employed in the presence of zinc oxide, the active agent is the zinc salt.[15] In the case of Classes 1 to 4 the zinc salt is the substance originally introduced or is formed easily by reaction with zinc oxide. In the case of Class 5 the zinc salt is formed, according to Maximoff, by reaction with zinc oxide, and according to Bedford, by reaction with hydrogen sulfide and zinc oxide.

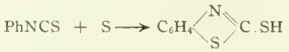
Other evidence supports the view that the zinc salts, and not the disulfides, are the active agents. Bedford supposes that the zinc salts function through the formation of polysulfides. While this is not improbable, there is as yet little direct experimental evidence in favor of this belief.

REACTIONS OF OTHER ACCELERATORS

Bruni and Romani have with some ingenuity sought to bring a large number of other types of accelerators within the same scheme as that which they propose for Classes 1 to 5, but all their suggestions call for closer investigation before they can be accepted. These authors give the following scheme for thiocarbanilide:

> Under the influence of heat the accelerator breaks down into phenyl mustard oil and aniline. The phenyl mustard oil then reacts with sulfur to give mercaptobenzothiazole, which, in the manner already suggested, is converted into the disulfide.

$$SC(NHPh)_2 \longrightarrow PhNH_2 + PhNCS$$



$$PhNCS + S \longrightarrow C_6H_4\begin{matrix}\diagup N \diagdown\\ \diagdown S \diagup\end{matrix}C.SH$$

Since mercaptobenzothiazole can also be obtained by the action of sulfur on other disubstituted thioureas, on mono- and on trisubstituted thioureas, on dimethylaniline, and on methyleneaniline, Bruni and Romani consider that the accelerating action of all these substances can be brought into the same scheme. Romani[16] has suggested that the mode of action of accelerators, such as aldehyde ammonia, hydrobenzamide, and furfuramide, formed by the condensation of an aldehyde with ammonia, can be similarly envisaged. He suggests that such substances give rise to the aldehyde and ammonia, that the ammonia forms polysulfides with hydrogen sulfide generated during vulcanization,[17] and that the polysulfides form a dithio acid (accelerator of Class 3) with the aldehyde.

The case of thiocarbanilide has also been discussed by others. Kratz, Flower, and Coolidge[18] concluded that its action is dependent essentially upon the aniline formed by its decomposition into aniline and phenyl mustard oil. They considered the latter substance to be inactive.[19] Bedford and Sebrell[6] believe that thiocarbanilide accelerates vulcanization by reacting, in its tautomeric form, $PhN{:}C(SH).NHPh$, to form a zinc mercaptide, which, as in the case of Classes 1 to 5, they believe to be the active substance. These authors state that the formation of mercaptobenzothiazole from thiocarbanilide under the influence of heat and sulfur does not occur, as the views of Bruni and Romani would demand, at the temperature of vulcanization. They quote some suggestive experiments in support of their view.

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[9] A point of some importance here is not clear—that is, whether such disulfides when used in the absence of free sulfur require zinc oxide to bring out their full curing power. Romani [*Giorn. chim. ind. applicata*, **3**, 197 (1921)] states that vulcanization by thiuram disulfides in the absence of free sulfur is rendered more energetic by the addition of zinc oxide, whereas Bedford and Sebrell [THIS JOURNAL, **14**, 25 (1922)] state that zinc oxide does not enhance the activity of these compounds.

[10] So far as the writer knows, it has not been experimentally demonstrated that the disulfides undergo conversion to monosulfides when heated. The method which has been used in the laboratory for this conversion has been treatment with potassium cyanide. Further, Bruni and Romani do not make it clear whether, when vulcanization is conducted in the presence of free sulfur, they regard the monosulfide, which they believe to be formed, as combining with sulfur to regenerate the disulfide and so activate the free sulfur. Vulcanization with a disulfide takes place much more quickly in the presence of zinc oxide and free sulfur than in the presence of zinc oxide alone. Furthermore, the monosulfides, although not quite so active as the disulfides, are, as Whitby and Simmons have recently found, powerful accelerators in the presence of zinc oxide.

In any case the question arises—what is the constitution of such organic disulfides? Are they Y.S.S.Y. or $Y.\overset{S}{\underset{S}{:}}Y$? If the former, the suggestion that they can split off sulfur and give monosulfides is less credible than if the latter. Their formation from thioles by oxidation would appear to indicate the former formula, whereas their conversion to monosulfides by treatment with potassium cyanide would appear to indicate the latter.

Bedford and Sebrell [THIS JOURNAL, **14**, 25 (1922)] agree with Bruni and Romani to the extent of concluding that one-quarter of the total sulfur of thiuram disulfides is available for vulcanization.

[11] THIS JOURNAL, **14**, 25 (1922).

[12] Whitby and Simmons, in a paper presented before the Division of Rubber Chemistry, at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[13] *Le Caoutchouc*, **18**, 10986 (1921).

[14] *Ibid.*, **18**, 10944, 10986 (1921).

[15] Earlier Bedford and Scott [THIS JOURNAL, **12**, 31(1920)] had expressed a different view as to the mode of action of dithiocarbamates. They supposed that at vulcanizing temperatures such compounds as the piperidinium salt of pentamethylenedithiocarbamic acid and the dimethylammonium salt of dimethyldithiocarbamic acid lose hydrogen sulfide to give thioureas. Apparently, at this time the important relation of zinc oxide to such accelerators was not recognized.

[16] *Le Caoutchouc*, **19**, 11626 (1922).

[17] This reaction has been described as a method of preparing dithio acids by Bruni and Levi [*Atti accad. Lincei*, [5] **32**, 5 (1923)].

[18] THIS JOURNAL, **12**, 317 (1920).

The ideas of Bedford have undergone much modification during their development, but his final belief apparently is that most cases of acceleration are due to polysulfide formation on the part of the thiole[20] or disulfide[21] groups.

Some investigators[14,11] hold that an important factor in the ability of certain compounds containing an —SH group to act as accelerators and of certain metallic oxides to "activate" such compounds is the stability of the mercaptides in question. Yet recent experiments[22] show that, although the heavy metal salts of accelerators in Classes 1 to 4 are distinguished in general by remarkable stability, the mere ability to form mercaptides, even of zinc, which are stable at vulcanizing temperatures is not enough to confer accelerating power, as some stable mercaptides, such as zinc phenylthiobiazolthione mercaptide, have little or no accelerating power.

DISPERSING AGENTS AS ACCELERATORS

Recent experiments[23] have introduced a new factor for consideration with respect to the mechanism of accelerator action. They make it appear that in some cases accelerators may owe part or all of their effect on the rate of vulcanization, not to action on the sulfur, but to action on the caoutchouc.[24] It has been shown that soaps hasten vulcanization in the presence of recognized vulcanization accelerators.[25] Their effect is presumably to increase the degree of dispersion of the caoutchouc, or of its sulfur reaction product.

Many accelerators are bases,[26] others, like aldehyde ammonia, may give rise to bases by decomposition; and others, like piperidinium pentamethylenedithiocarbamate, may give rise to bases as a result of reaction with zinc oxide. Such bases, if sufficiently strong, will give rise to soaps by neutralizing the acids of which the rubber resin has recently been shown largely to consist.[27] The formation of soaps in this way not only increases the rate of vulcanization, but also leads to enhanced tensile strength in the vulcanized product.[28]

The action of an accelerator such as piperidinium pentamethylenedithiocarbamate is believed to depend upon the formation of two substances—(1) the zinc dithiocarbamate, and (2) piperidinium salts (soaps) of the resin acids. Representing the acids of the rubber resin as HA, the reactions which probably occur in a rubber stock containing zinc oxide and an accelerator of the type just mentioned may be shown as follows:

$$2C_5H_{10}N.CS.SNH_2C_5H_{10} + ZnO + 2HA \longrightarrow (C_5H_{10}N.CS.S)_2Zn + 2A.NH_2C_5H_{10} + H_2O$$

It is probable that some of the phenomena in rubber which have been described as "depolymerization" and "polymerization" are in reality merely changes, such as those caused by the introduction of soaps, in the degree of dispersion of the caoutchouc.

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[19] Whitby and Dolid (paper presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923) have found that mustard oils dissolve rubber to give strikingly limpid solutions. It is therefore possible that, although mustard oils may not accelerate vulcanization by activating sulfur, they may do so by increasing the degree of dispersion of caoutchouc.

[20] The —SH group may be originally present in the molecule, as in the case of Classes 1 to 4, or it may be formed by tautomerization, as in the case of thiocarbanilide. Whitby and Simmons report that in general where the occurrence of an —SH group depends upon tautomerization, accelerating power is absent or comparatively low. In an earlier paper [Scott and Bedford, THIS JOURNAL, **13**, 125 (1921)] it was suggested that in the case of a large number of accelerators —SH groups arise by the addition of hydrogen sulfide to ammonia or an amine, and such accelerators were described as "hydrogen sulfide polysulfide" accelerators. But apparently this suggestion has been modified or abandoned.[6]

[21] In some cases disulfides are supposed to be formed by sulfur reaction. Yet, while in the case of accelerators of Class 5, acting in the presence of zinc oxide, this author regards disulfides as being reduced to thioles prior to polysulfide formation, in the case of the disulfides which he regards as being formed by sulfur reaction from such accelerators as aromatic diamines,[6] and in the case of accelerators of Class 5, acting in the absence of zinc oxide,[11] he regards the disulfides themselves as undergoing polysulfide formation.

[22] Whitby and Simmons, *loc. cit.*; Whitby, *Roy. Soc. Canada*, May, 1923

[23] Whitby and Cambron, *J. Soc. Chem. Ind.*, **42**, 333T (1923); Whitby and Simmons, *loc. cit.*

[24] Some indirect evidence for the view that accelerators may affect the rubber rather than the sulfur was advanced by Le Blanc and Kröger [*Z. Elektrochem.*, **27**, 335 (1921)]. These authors found, in experiments on the rate of gel formation in rubber-sulfur cements, that solvents of high dielectric constant, giving rubber solutions of low viscosity (solutions in which the rubber is "depolymerized"), led to a more rapid gelling than solvents of lower dielectric constant, giving solutions of higher viscosity, and that accelerators both reduced the viscosity and hastened gel formation.

[25] Ultra-accelerators were used, but it is probable that soaps have a similar effect on vulcanization in the presence of milder accelerators and of the accelerators naturally present in raw rubber.

[26] Caustic alkalies act as vulcanization accelerators. Twiss [*J. Soc. Chem. Ind.*, **36**, 782 (1917)], who is responsible for the most complete study of caustic alkalies as accelerators, mentioned the possibility of such accelerators functioning by acting on the rubber rather than on the sulfur. Twiss and Thomas [*Ibid.*, **40**, 48T (1921)] disproved the suggestion that the accelerating action of caustic alkalies and other bases is due to their catalytic effect on the transformation of S_μ into S_λ. Scott and Bedford [THIS JOURNAL, **13**, 125 (1921)] regarded caustic alkalies as functioning through the formation of polysulfides on the part of the hydrosulfides supposed to arise from them by the action of hydrogen sulfide. Bedford and Sebrell[6] considered the action of sodium phenolates as accelerators to be due to reaction of sulfur with the aromatic nucleus leading to a disulfide—for example, $NaO.C_6H_4.S.S.C_6H_4.ONa$, from which polysulfides are formed.

[27] Whitby and Winn, *J. Soc. Chem. Ind.*, **42**, 336T (1923).

[28] This observation may prove to be of significance with regard to the question of the structure of elastic gels.

Huge Sale of Pulp Timber by Forest Service

The largest sale of pulp timber ever made by the United States Forest Service was announced recently. The transaction involves 334,000,000 cubic feet of timber in the Tongass National Forest, Alaska. The buyer, the firm of Hutton, McNear & Dougherty, of San Francisco, has agreed as part of the consideration for the timber to build a pulp manufacturing plant of not less than 100 tons daily capacity, and ultimately with a daily capacity of 200 tons, at the Cascade Creek water-power site on Thomas Bay, 20 miles from Petersburg, Alaska, within the Tongass National Forest. It is understood that the firm plans to instal a complete newsprint plant with a daily capacity of 200 tons.

According to the plans of the Forest Service for this sale unit, as well as for all pulp timber developments in Alaska, the timber will be cut on a perpetual supply basis, enough seed trees being left to insure complete natural reproduction. The volume of pulp timber and the area of timber-growing land within the unit, reserved from other disposition, are sufficient to afford a permanent source of raw material for this enterprise.

Under the perpetual timber supply plan at least 1,500,000 tons of paper can ultimately be produced in Alaska every year. This amount is more than one-half of the newsprint now consumed annually in the United States and nearly 20 per cent of the total consumption of all kinds of paper and wood fiber products. As each new unit of timber and water power is developed in Alaska, the manufacturing capacity will be gaged to the timber supply and growing power of the land so that there will be no depletion of raw material.

The Cascade Creek sale is in line with the policy for the development of the national forest in Alaska, which was a subject of special study by President Harding during his trip to the Territory and which received his indorsement.

1—Mercaptobenzothiazole and Its Derivatives as Accelerators of Rubber Vulcanization[1,2,3]

By L. B. Sebrell and C. E. Boord

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In a separate paper[2] the preparation and properties of 1-mercaptobenzothiazole and six of its substituted derivatives have been fully described. Three of these methods are new. The mechanism of the reactions involved in these preparations has been fully discussed. For six of these mercaptothiazoles the disulfides have also been described, and in two cases the zinc and lead salts.

Mercaptobenzothiazole and its substituted derivatives show the following relative activity as accelerators of vulcanization: (1) 3-methyl, (2) 3,5-dimethyl, (3) unsubstituted, (4) 4-methyl, (5) 5-methyl, (6) 5-ethoxy, (7) 5-methoxy. Several compounds with a structure analogous to 1-mercaptobenzothiazole were prepared and their accelerating values determined. The mercaptobenzothiazoles have no value as accelerators except in the presence of zinc oxide. The zinc and normal lead salts of these thiazoles are faster curing than the corresponding free thiazoles. The zinc salt of the 1-mercapto-5-methylbenzothiazole and the normal lead salt of 1-mercapto-3-methylbenzothiazole gave the highest accelerating values of any of the compounds tested. The disulfides have a lower curing power than the corresponding free thiazoles. The accelerating power of the mercaptobenzothiazoles is directly connected with the atomic grouping $—S—\overset{\|}{C}—SH$. *Any alteration in this grouping removes almost entirely the power to accelerate rubber vulcanization. The mercapto group is more essential to the accelerating action than the sulfur atom of the thiazole ring. Both are necessary to develop the highest accelerating power. Aliphatic mercaptothiazoles show marked accelerating power but are inferior to the mercaptobenzothiazoles. The metallic salts of the mercaptobenzothiazoles are assumed to be the active agents in producing acceleration.*

The existing theories for the mechanism of acceleration by mercapto compounds have been given. The results obtained in this work are correlated with the Bedford and Sebrell polysulfide theory.

THE use of 1-mercaptobenzothiazole as an accelerator of vulcanization was first suggested by Bedford and Sebrell.[4] This announcement was closely followed by that of Bruni and Romani,[5] who set forth in detail a method for the preparation of 1-mercaptobenzothiazole by heating thiocarbanilide with sulfur under pressure. They also proposed a theory for the mechanism of the accelerating action as applied to thiocarbanilide and the thiazole derivatives.

The second paper of Bedford and Sebrell[6] revealed that the method of preparation described by Bruni and Romani had previously been known to them, and pointed out that the mechanism used by the latter workers to explain the action of thiocarbanilide as an accelerator was untenable.

The present investigation is a continuation of the work of Bedford and Sebrell. It has been carried out with the following purposes in mind:

1—To make a comparative study of the relative value of several derivatives of 1-mercaptobenzothiazole as accelerators of vulcanization.

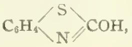
2—By a process of substitution and elimination to determine what part of the mercaptobenzothiazole structure is responsible for the accelerating action of these compounds.

Preparation of Materials

1-Mercaptobenzothiazole and Its Derivatives—The preparation and properties of 1-mercaptobenzothiazole and its 3-methyl, 4-methyl, 5-methyl, 3,5-dimethyl, 5-methoxy, and 5-ethoxy derivatives have been fully described in a separate paper by the present authors.[2] Each of these compounds, with two exceptions where the quantity of material was limited, was prepared by four methods. The methods were all alike in that the reaction mixtures were heated together in an autoclave under pressure. The mixtures were (1) the corresponding disubstituted thiourea and sulfur, (2) the zinc salt of the corresponding aryldithiocarbamic acid and sulfur, (3) the ammonium salt of the same acid and sulfur, and (4) a mixture of the corresponding aryl amine, carbon disulfide and sulfur.[7]

The first of these methods is the same as used by Bedford and Sebrell[4] and by Bruni and Romani[5] to prepare 1-mercaptobenzothiazole. It was extended by the present authors[8] and also by Romani[9] to the monomethyl derivatives of this same thiazole. The disulfides of the unsubstituted thiazole and each of its methylated derivatives were described, as well as the normal zinc, normal lead, and basic lead salts of the same thiazole and its 3-methyl derivative and the normal zinc salt of the 5-methyl derivative. For the details of these preparations it will be necessary to consult the original article.

Other Benzothiazole Derivatives—In order to determine the particular grouping in the 1-mercaptobenzothiazole structure responsible for the accelerating action, it became necessary to prepare a series of related benzothiazole derivatives. In each case these compounds differed from the true 1-mercaptobenzothiazole by a single atom or grouping, the remaining part of the molecular structure being identical. All these substances have been previously described, but the details of their preparation are incomplete.

1-Hydroxybenzothiazole,[10]  $C_6H_4\langle{}^{S}_{N}\rangle COH$, was prepared

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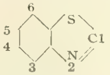
[1] Presented before the Division of Rubber Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] This paper and one entitled: "The Preparation and Properties of 1-Mercaptobenzothiazole; Its Homologs and Derivatives," being published simultaneously in *J. Am. Chem. Soc.*, **45**, 2390 (1923), have been abstracted from the dissertation presented by L. B. Sebrell to the Graduate School of Ohio State University in partial fulfilment of the requirements for the degree of doctor of philosophy, September, 1922.

[3] The remarks of Bogert and Meyer, *J. Am. Chem. Soc.*, **44**, 826 (1922), concerning the numbering and nomenclature of the benzothiazole derivatives, have been noted with some interest. Their contention that all the atoms of the thiazole ring should be numbered is correct, but for the sake of uniformity the present authors prefer to adhere to the system in use by *Chemical Abstracts*. For this reason, the system as outlined by Decennial Index of *C. A.*, **1**, 2345 (1907–1916)—namely, omitting the sulfur and beginning the numbering with the carbon atom of the thiazole ring—has been followed.



[4] This Journal, **13**, 1034 (1921).

[5] *Giorn. chim. ind. applicata*, **3**, 196 (1921).

[6] This Journal, **14**, 25 (1922).

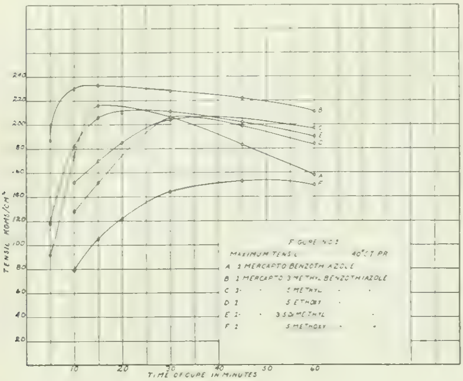
[7] This method was suggested by W. J. Kelly of the Goodyear Tire & Rubber Company.

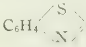
[8] *Science*, **56**, 55 (1922).

[9] *Gazz. chim. ital.*, **52**, 29 (1922).

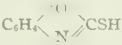
[10] *Ber.*, **12**, 1126 (1879); **13**, 9 (1880).

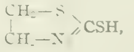
by the hydrolysis of 1-chlorobenzothiazole, according to the method described by Hofmann.[10] Long heating of the free 1-chlorobenzothiazole does not accomplish the hydrolysis. However, if the hydrogen chloride addition product of 1-chlorobenzothiazole is heated with alcohol for 40 hours, the hydrolysis is almost complete. The solution was rendered strongly acid and precipitated by dilution with water. After two recrystallizations from 75 per cent alcohol 1-hydroxybenzothiazole was obtained as white needles melting at 136° C. This is the same melting point as given by Hofmann. The hydrolysis of the hydrochloride may be accomplished in a much shorter time by heating with alcohol under pressure.



1-Amidobenzothiazole,  $C_6H_4\Big\langle\begin{matrix}S\\N\end{matrix}\Big\rangle C{-}NH_2$, was first prepared by Hofmann[11] by the action of alcoholic ammonia on 1-chlorobenzothiazole at 160° C. In this laboratory the method, as described, always yields the product in the form of a noncrystallizable sirup. Excellent results were obtained by the following method:

Fifteen grams of the 1-chlorobenzothiazole together with 45 cc. of saturated alcoholic ammonia and 15 cc. of aqueous ammonia were sealed in a tube and heated at 200° C. for 4 hours. On opening the tube the contents were mixed with 50 per cent alcohol, strongly cooled in an ice bath and diluted very slowly with water to 1 liter. After standing in an ice box for 12 hours 1-amidobenzothiazole was deposited as fine white needles, with only a trace of the sirupy impurity. The yield was 10 grams. This product after recrystallization from benzene melted at 127° C., compared with 129° C. recorded by Hofmann.

1-Mercaptobenzoxazole,  $C_6H_4\Big\langle\begin{matrix}O\\N\end{matrix}\Big\rangle CSH$, was prepared by refluxing an alcoholic solution of *o*-aminophenol with carbon disulfide according to the method of Dünner.[12] After the preliminary purification by precipitating from sodium carbonate solution, and recrystallization from water, the product melted at 193° C., the same as recorded by Dünner.

μ-Mercaptothiazolen,  $\begin{matrix}CH_2{-}S\\|\\CH_2{-}N\end{matrix}\Big\rangle CSH$, was prepared for the purpose of comparison with 1-mercaptobenzothiazole to determine the effect of the aromatic nucleus upon the accelerating power of the mercaptothiazoles. The compound was first described by Gabriel[13] who prepared it by the action of *β*-bromoethylamine hydrochloride and carbon disulfide in alkaline solution. Some difficulty was experienced in the isolation of both the hydrobromide and its reaction product with carbon disulfide, but a sufficient quantity was finally obtained to determine its relative value as an accelerator.

RESULTS OF COMPOUNDING TESTS

All the compounds listed above were tested to ascertain their relative value as accelerators of vulcanization. The following experimental formula was used:

100.00	parts of rubber (smoked sheet)
5.00	parts of zinc oxide
3.50	parts of sulfur
1.00	part of 1-mercaptobenzothiazole or a molecular equivalent of its derivative or analog

With a few exceptions, each of these compounds produced very rapid curing in the formula given.

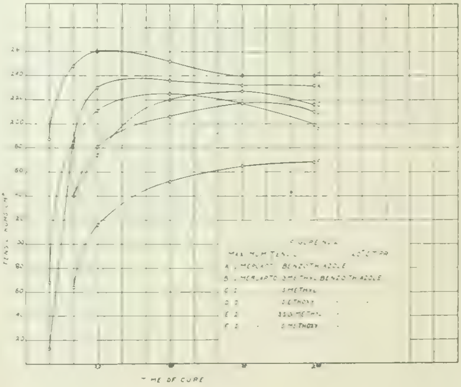
Since many of these substances are rapid and powerful accelerators, slight variations in the milling and curing may produce differences of some magnitude in the tensile-time diagrams. For this reason the conditions of milling and curing were standardized as follows:

The stocks were all mixed in 1-kg. batches on a small experimental mill. After milling for 20 minutes to break down the rubber, the zinc oxide and accelerator were added and mixed thoroughly into the stock for 10 minutes. The stock was then cooled to the lowest workable temperature and the sulfur added. After 5 minutes further mixing it was removed from the mill. All samples were milled as nearly as possible as described above.

The curing was conducted in a steam platen press in which the temperature was controlled as closely as possible. All cures were made in the same set of molds, which had been preheated before use by allowing them to remain for at least 30 minutes in the press at the required temperature. All the cures were made using the same decks of the same press. The vulcanized sheets after being removed from the molds were plunged into a tank of cold water to stop vulcanization.

The physical data given in the following tables were obtained by two observers on a Scott testing machine using dumb-bell test pieces. The average of two or more closely agreeing strips is given for each cure.

The results of the physical tests on the cures made with 1-mercaptobenzothiazole, its alkyl and alkyloxy derivatives, are recorded in Table I, and are represented graphically in Figs. 1 and 2. In comparing the relative activity of these compounds, the writers have used as a basis of comparison the time in which each compound was judged to give the best technical cure. This can best be determined by subjecting the stocks themselves to certain arbitrary tests, such as the effect of repeated flexing and resistance to tear. The nature of the grain as indicated by the appearance of the tear is also



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[11] *Ber.*, **13**, 11 (1880).

[12] *Ibid.*, **2**, 465 (1876); **16**, 1825 (1883).

[13] *Ibid.*, **21**, 566 (1888); **22**, 1137, 1152 (1889).

TABLE I—PHYSICAL TESTS—STOCKS CURED WITH MERCAPTOBENZOTHIAZOLES

ACCELERATORS	Time of Cure Min	100%	200%	300%	400%	500%	600%	700%	800%	Bk	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
40 pounds steam pressure (141° C.)														
1-Mercaptobenzothiazole	5	2.5	3	4	6	7	12	21	48	92	900	82.8	149.5	Under
	10	4	7	10.4	16	24	46	105	160	174	810	141.0	309	Best
	15	5	12	15	23	33	70	140		216	780	168.5	370	Slightly over
	30	4.5	8	13	20	36	75	150		206	780	161.0	374	Over
	45	5	9	12.5	21	34	66	125		183	770	141.0	318	Over
	60	5	9	12	19	34	55	114		158	770	121.7	286	Over
1-Mercapto-3-methylbenzothiazole	5	5	7	12	18	26	58	124	187	187	800	149.5	343	Slightly over
	10	7	10	17	25	43	85	167	...	230	780	179.5	330	Slightly over
	15	7	11	17	24	46	84	165		233	750	175.0	371	Over
	20	7	11	17	24	40	83	152		224	780	175	408	Over
	30	6	10	14	24	39	73	154		228	750	170	338.5	Over
	45	6	10	16	24	45	83	161		222	780	173	418	Over
	60	5	7	12	19	30	54	112		211	800	169	344	Over
1-Mercapto-5-methylbenzothiazole	10	4	5	7	12	15	27	65	122	152	860	131	278	Under
	15	4	6	8	12	19	36	82	151	170	830	141	290.6	Slightly under
	20	5	6	11	14	24	46	100	177	185	810	150	312.6	Very slightly over
	30	4	7	12	17	25	46	138	...	204	780	159	317	Very good over
	45	5	8	12	18	30	60	127	...	193	780	150.5	320.5	Over
	60	5	7	12	18	30	66	114	183	197	820	161	381.5	Over
1-Mercapto-5-ethoxybenzothiazole	10	4	6	8	12	17	28	58	99	128	850	109	239	Under
	15	4	6	11	15	24	44	95	149	157	815	128	296	Very slightly under
	30	4	7	14	18	31	62	124	206	206	800	165	363	Over
	45	5	8	12	19	31	60	123	199	199	800	159	358	Over
	60	5	7	12	18	25	47	94	166	184	825	152	335	Over
1-Mercapto-5-methoxybenzothiazole	10	1	3	4	5	7	12	19	36$\frac{900}{72}$	79	975	105	179.6	Under
	15	3	4	6	7	12	18	36	66	106	900	94.5	204	Under
	20	4	5	7	10	15	24	47	90	121	860	104	220	Under
	30	4	6	10	12	23	42	83		144	780	112	230	Under
	45	3	6	9	14	20	34	69	132	153	860	132	306.5	Fair
	60	4	6	10	12	22	40	78	144	150	820	123	273	Good
1-Mercapto-3-5-dimethylbenzothiazole	5	3	4	6	7	11	18	32	74	118	890	105	204	Under
	10	5	6	11	16	23	46	108	172	182	810	143	319	Very slightly over
	15	4	6	11	17	25	50	120	206	206	800	165	336	Over
	20	5	9	14	23	39	77	142	...	210	780	164	379	Over
	30	5	10	13	21	38	77	149	211	211	800	169	419	Over
	45	5	7	12	18	30	54	113	178	202	825	167	375.5	Over
	60	6	7	12	19	30	69	108	...	190	790	150	321	Over
20 pounds steam pressure (125° C.)														
1-Mercaptobenzothiazole	10	1	2	3	4	5	6	8	12	13	820	10.7	60	Under
	20	4	6	10	15	21	41	78	152	184	845	155	326.6	Slightly under
	30	5	8	14	20	31	68	135	230	230	800	184	401	Best
	60	5	10	16	24	44	90	174	...	236	760	179	399	Over
	90	5	10	16	25	44	92	174	...	232	770	178	421	Much over
	120	5	10	17	25	46	87	173		232	770	178	417	Much over
1-Mercapto-3-methylbenzothiazole	10	4	8	10	16	22	41	89	168	187	830	155	318	Slightly under
	20	5	10	16	24	40	75	146	...	248	790	196	320	Slightly over
	30	6	12	19	29	50	103	205	...	260	750	195	437	Over
	60	6	11	19	31	54	110	214	...	252	740	187	431	Over
	90	6	14	20	30	50	110	216	...	240	730	175	406	Much over
	120	6	14	20	30	54	110	187	...	240	730	175	391	Much over
1-Mercapto-5-methylbenzothiazole	20	3	5	8	10	15	26	47	93	140	900	126	277	Under
	30	5	8	10	15	25	48	99	174	174	800	139	337	Under
	60	5	10	16	21	33	76	144		220	790	166	397	Good, slightly over
	90	5	10	15	24	38	74	150	...	227	790	172	410	Over
	120	5	10	15	25	42	76	166		213	760	162	369	Over
1-Mercapto-5-ethoxybenzothiazole	20	3	5	8	10	15	26	50	101	140	890	125	276	Under
	30	5	6	10	14.5	21	35	75	146	182	860	157	338	Slightly under
	60	5	10	12	20	31	62	135		195	770	150	323	Best
	90	5	10	15	22	35	71	134		218	770	168	348	Over
	120	5	10	15	24	41	85	152		210	780	164	401	Over
1-Mercapto-5-methoxybenzothiazole	20	2	3	4	5	6	10	16	25	64	980	62.7	139	Very much under
	30	3	4	5	8	12	21	40	72	116	900	105	223	Much under
	60	5	7	10	15	21	36	78	136	142	830	118	282	Fair
	90	4	6	10	16	25	46	93		165	800	132	283	Fair
	120	5	9	15	20	30	54	108		168	780	131	297	Best
1-Mercapto-3-5-dimethylbenzothiazole	10	2	3	4	5	7	11	18	34	68	940	64	136	Under
	20	4	8	12	17	25	56	112		185	790	146	312	Good, slightly under
	30	6	10	15	21	36	74	153	...	211	765	162	475	Good, slightly over
	60	5	10	16	26	46	102	200	...	225	740	167	390	Over
	90	5	10	18	27	48	98	185		194	720	140	336	Much over
	120	5	10	16	26	46	92	183	...	199	740	147	363	Much over

taken into consideration. The results of such tests are given for each cure in the tables in the column "State of Cure." In some cases the cures were not sufficiently close so that, for example, a 5-minute cure might be judged by means of these tests to be undercured, while a 10-minute cure would be considerably overcured. In such cases the writers have interpolated for the time of best technical cure.

The relative order of activity of these compounds as accelerators cannot well be determined from a comparison of the maximum tensiles obtained, since the test sheet which would give the highest tensile is in almost all cases overcured from a practical standpoint. Any attempt to classify the compounds on the basis of the so-called optimum cure, as given by either the maximum tensile product or the energy of resilience, or a combination of these factors, would be subject to the same objection as given above for the classification in order of maximum tensile.

If it is desired to utilize the stress-strain data in determining the relative activity of these compounds, they can, for example, be ranked in the order of the highest tensile stress at 700 per cent elongation given by a 10-minute cure on each compound at 40 pounds steam pressure. In this way the errors inherent in a determination of the maximum tensile are avoided. If such a classification is made it will be found that the compounds arrange themselves in exactly the same order as determined by the best technical cure.

The writers are therefore inclined to classify the various mercaptobenzothiazoles according to the time necessary to produce the best cure from a practical standpoint as shown by the above arbitrary tests, and to use the stress-strain data as a measure of the quality of the stocks.

It is realized that the present method of determining the relative activity might not seem satisfactory to all, and for this reason the complete data for the physical tests, together with the tensile product and the energy of resilience, have been included in the tables.

Since only one formula was used in testing all these accelerators and because in some cases an insufficient number of cures have been obtained, it is obvious that the results herein presented cannot be considered as representing a complete or detailed compounding investigation. They are, however, considered satisfactory from the standpoint of determining the relative activity of the various mercaptobenzothiazoles and their derivatives as accelerators.

Fig. 1 shows the tests made on cures at 40 pounds steam pressure, while Fig. 2 gives the same data for cures at 20 pounds steam pressure. The relative activity of the 1-mercaptobenzothiazoles and the time required to produce the best technical cure are given in Table II.

TABLE II—ORDER OF REACTIVITY OF THE 1-MERCAPTOBENZOTHIAZOLES AS ACCELERATORS

SUBSTANCE	40 Pounds Pressure		20 Pounds Pressure	
	Time of Best Technical Cure	Order of Activity	Time of Best Technical Cure	Order of Activity
1-Mercapto-3-methylbenzothiazole	5 min.	1	18 min.	1
1-Mercapto-3,5-dimethylbenzothiazole	8 min.	2	25 min.	2
1-Mercaptobenzothiazole	10 min.	3	30 min.	3
1-Mercapto-5-methylbenzothiazole	18 min.	4	55 min.	4
1-Mercapto-5-ethoxybenzothiazole	20 min.	5	60 min.	5
1-Mercapto-5-methoxybenzothiazole	1 hr.	6	2 hrs.	6

The data showing the relative curing power of 1-mercapto-4-methylbenzothiazole are not given in Table II. A limited supply of this material prevented it from being included when the foregoing tests were made. It had previously been tested in a different formula. Under these conditions its activity as an accelerator was found to lie between the 5-methyl and 3-methyl derivatives, being very close to that of 1-mercaptobenzothiazole.

In the absence of zinc oxide the 1-mercaptobenzothiazoles are without appreciable accelerating action. Compounded in the foregoing formula, except that the zinc oxide was omitted, 1-mercaptobenzothiazole cured at 40 pounds steam pressure for 2 hours gave a maximum tensile strength of 96 kg. per sq. cm. Curing the same mixture at 20 pounds steam pressure for the same time gave a maximum tensile strength of 50 kg. per sq. cm. These substances, therefore, have no practical value as accelerators except in the presence of zinc or lead oxides. From these results it seems probable that in the process of vulcanization the mercaptobenzothiazoles are converted into the corresponding zinc salts, these salts acting as the true accelerating agents. To test this assumption the zinc and lead salts of 1-mercapto-, 1-mercapto-3-methyl, and 1-mercapto-5-methylbenzothiazoles were tested in the foregoing formula. The results are shown in Tables III*a* and III*b* and the tensile–time curves in Figs. 3 and 4.

The zinc salt of the 5-methyl derivative is slightly faster in its curing action than the zinc salt of the free 1-mercaptobenzothiazole or its 3-methyl derivative. The last two are about equal in curing power. On the other hand, the lead salt of the 3-methyl derivative is the most active of the three lead salts, giving good cures in 15 minutes at 20 pounds steam pressure. The two remaining lead salts are about equal in activity but vary in the tensile strengths produced.

In all cases the zinc and lead salts of these mercaptobenzothiazoles are much more powerful accelerators than the corresponding free compounds. The zinc salt is, generally, more powerful than the corresponding lead salt. These metallic salts must also be used with additional metallic oxide to obtain their maximum accelerating power.

The disulfides of the several mercaptobenzothiazoles were also tested in the foregoing formula, and were found to be considerably less active than the free thiazoles.

Two conclusions may be drawn from these facts:

1—The 1-mercaptobenzothiazoles when used as accelerators first form the metallic salts by action with the metallic oxide present. These salts are the active accelerators.

2—The salts so formed tend to decompose during the process of vulcanization and an excess of the metallic oxide must be present to reform the salts and thus maintain the accelerating action.

TABLE III*a*—PHYSICAL TESTS: STOCKS CURED WITH THE ZINC SALTS OF MERCAPTOBENZOTHIAZOLE

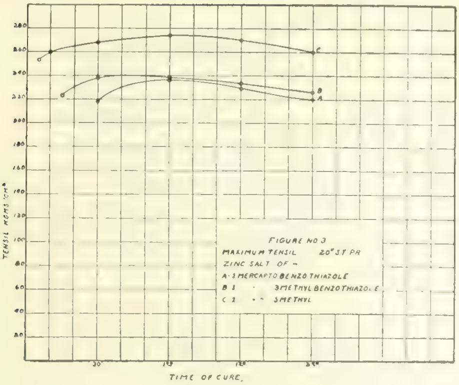
20 pounds steam pressure (125° C.)

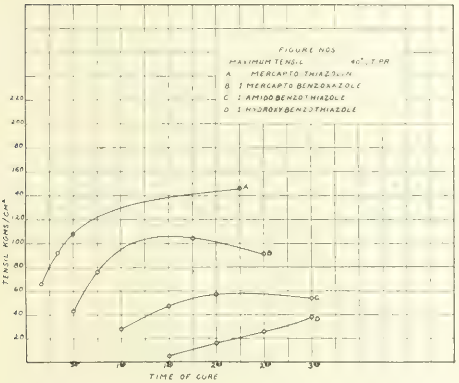
ACCELERATOR	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
1-Mercaptobenzothiazole	30	8	13	20	29	52	109	202	. .	218	720	155	374	Over
	60	8	14	22	36	64	127	221	. . .	236	715	169	415.8	Over
	90	9	14	23	39	67	130	219	. . .	229	715	163	425	Over
	120	9	14	23	37	64	125	206	. . .	220	720	158	417.6	Over
	180	8	14	21	33	55	106	188	. . .	210	720	151	370.8	Over
1-Mercapto-3-methylbenzothiazole	15	6	10	15	39	53	104	198	. .	223	750	167	431	Good
	30	6	11	21	38	73	141	219	. .	238	740	167	490.9	Over
	60	6	12	21	36	62	120	218	. .	238	730	174	434.4	Over
	120	6	12	18	32	57	108	200	. . .	226	740	167.5	418	Over
	180	6	12	19	33	57	107	190	. . .	220	740	163	493	Over
1-Mercapto-5-methylbenzothiazole	5	5	9	13	21	37	67	133	220	253	825	204	454	Slightly under
	10	5	9	13	22	40	80	142	. . .	260	855	222	350.5	Under
	30	6	10	18	26	52	102	183	. . .	268	850	228	418	Over
	60	6	12	20	30	60	114	208	. . .	274	745	204	454	Over
	120	6	13	20	34	62	114	211	. . .	260	730	190	425	Over
	180	5	10	20	32	60	104	185	. . .	238	760	181	450.4	Over

TABLE III*b*—PHYSICAL TESTS: STOCKS CURED WITH NORMAL LEAD SALTS OF MERCAPTOBENZOTHIAZOLES

20 pounds steam pressure (125° C.)

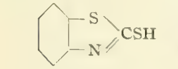
ACCELERATOR	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
1-Mercaptobenzothiazole	15	7	8	12	18	30	58	108	. . .	142	760	108	232	Good
	30	6	11	16	25	42	78	145	. . .	181	740	134	315.7	Over
	60	7	12	18	39	46	97	165	. . .	202	710	144	319.8	Over
	90	6	11	18	39	46	86	160	. . .	206	750	155	377.5	Over
	120	6	11	17	27	24	81	141	. . .	202	760	154	339.4	Over
	180	7	10	15	25	40	70	129	. . .	183	780	143	356	Over
1-Mercapto-3-methylbenzothiazole	15	5	9	16	26	45	92	162	250	260	835	217	551	Good
	30	5	9	17	27	46	97	175	. . .	255	752	192	400	Over
	60	7	11	17	28	48	102	186	. .	248	785	193	490.5	Over
	120	6	12	19	29	50	105	190	. . .	241	745	179	413	Over
	180	6	10	20	30	54	106	186	. . .	238	767	182	461	Over
1-Mercapto-5-methylbenzothiazole	10	3	5	7	9	10	18	36	60 $\frac{900}{100}$	113	960	108.5	261.9	Under
	25	5	9	14	20	25	60	120	. . .	180	790	142	328	Good
	60	5	10	16	26	41	88	164	. .	225	760	171	384.7	Over
	120	5	10	15	25	49	92	171	. . .	226	770	169	420	Over
	180	5	10	16	35	45	79	158	. . .	220	800	716	458	Over

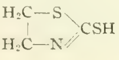


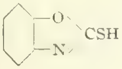


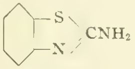
Tests on Compounds Similar to 1-Mercaptobenzothiazole

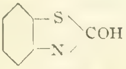
μ-Mercaptothiazoline (*A*), 1-mercaptobenzoxazole (*B*), 1-amidobenzothiazole (*C*), and 1-hydroxybenzothiazole (*D*) were also tested for their accelerating action. Each of these compounds resembles 1-mercaptobenzothiazole in certain parts of its structure. The results of these tests are recorded in Table IV and shown graphically in Fig. 5.


1-Mercaptobenzothiazole

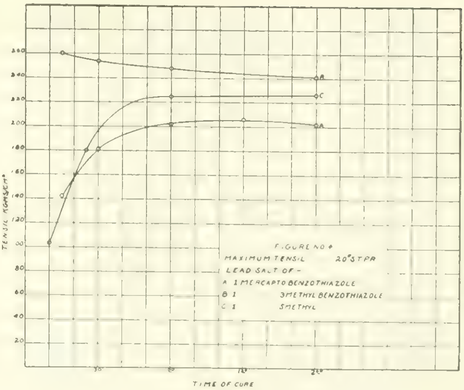

(*A*)


(*B*)


(*C*)


(*D*)

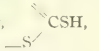
The results show that the μ-mercaptothiazoline exerts a marked accelerating action, but much less than that of 1-mercaptobenzothiazole. This would seem to indicate that the accelerating power is invested in the mercaptothiazole group. When the sulfur atom of the thiazole ring is replaced by oxygen as in 1-mercaptobenzoxazole, the accelerating action is still evident but much lower than that of either 1-mercaptobenzothiazole or μ-mercaptothiazoline.



If the mercapto group is replaced by an amino or an hydroxyl group, as in 1-amidobenzothiazole or 1-hydroxybenzothiazole, respectively, the accelerating action is very greatly diminished; indeed, in the latter substance it is almost entirely absent.

The conclusions to be drawn from these results are as follows:

1—The accelerating action of 1-mercaptobenzothiazole and its derivatives is invested primarily in the mercaptothiazole group. The presence of the benzene nucleus adds markedly to the accelerating value. Whether this is due to the attendant increase in the molecular weight or more directly concerned with the chemical characteristics of the benzene nucleus, is not yet determined.

2—The atomic grouping,  is directly responsible for the accelerating action. Any change in this grouping either greatly diminishes or completely destroys the accelerating value.

3—The mercapto group is more essential to the acceleration than the sulfur of the thiazole ring, although both are necessary to the best results.

Mechanism of Acceleration by Mercaptobenzothiazole Derivatives

Several theories have recently been advanced to explain the vulcanization of rubber by organic compounds containing the mercapto group. Bruni and Romani[5] have proposed the following mechanism for the acceleration of vulcanization by mercaptobenzothiazoles:

$$\begin{gathered}2\mathrm{R{-}SH} + \mathrm{ZnO} \longrightarrow (\mathrm{R{-}S})_2\mathrm{Zn} + \mathrm{H_2O}\\ x(\mathrm{R{-}S})_2\mathrm{Zn} + \mathrm{S}x \longrightarrow x\mathrm{R{-}S{-}S{-}R} + x\mathrm{ZnS}\\ \mathrm{R{-}S{-}S{-}R} \longrightarrow \mathrm{R{-}S{-}R} + \mathrm{S}\ (\textit{active})\end{gathered}$$

They have lately extended this theory to many other well-known accelerators, such as thiocarbanilide and aldehyde ammonia.[14] It is chiefly interesting as it applies to mercaptobenzothiazole derivatives. The disulfides are less active accelerators than the free mercaptobenzothiazoles, both with and without the presence of zinc oxide. In the absence of zinc oxide both types of derivatives are almost without accelerating power. These facts seem to show that the disulfide cannot be the active agent in this type of acceleration. The theory is therefore inadequate and cannot be accepted.

Bedford and Sebrell[6] have proposed a theory to account for the action of mercapto compounds as accelerators, which may be stated as follows:

$$\begin{gathered}2\mathrm{R{-}SH} + \mathrm{ZnO} \longrightarrow (\mathrm{R{-}S})_2\mathrm{Zn} + \mathrm{H_2O}\\ (\mathrm{R{-}S})_2\mathrm{Zn} + \mathrm{S}_x \longrightarrow (\mathrm{R{-}SS}_x)_2\mathrm{Zn}\\ (\mathrm{R{-}SS}_x)_2\mathrm{Zn} \longrightarrow (\mathrm{R{-}S})_2\mathrm{Zn} + \mathrm{S}\ (\textit{active})\end{gathered}$$

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[14] Romani, *Caoutchouc gutta-percha*, **19**, 11626 (1922).

TABLE IV—PHYSICAL TESTS STOCKS CURED WITH ANALOGS OF MERCAPTOBENZOTHIAZOLE

40 pounds steam pressure (141° C.)

ACCELERATOR	Time of Cure Min.	100%	200%	300%	400%	500%	600%	700%	800%	Bk.	Elong.	Tensile Product	Energy of Resilience	STATE OF CURE
μ-Mercaptothiazoline	10	1	2	4	6	8.5	10	20	34	66	900	59.4	68.5	Under
	20	3	4.5	6	9	14	19	35	66	92	895	82.3	197.5	Under
	30	2.5	5	6.5	9	14	23	45	85	108	870	94.0	215	Fair
	45	3.5	5	8	10	14	24	50	95	109	845	92	207.9	Fair
	60	3.5	5	8	11	16	28	48	96	104	825	86	192.5	Slightly over
	135	4	7.5	11	15	23	41	86	..	138	785	108	239.7	Over
1-Mercaptobenzoxazole	30	2	2.5	3.5	4.5	5.5	7	9	14	43	990	42.5	66.6	Under
	45	2	3	5	5.5	7	10	18	32	76	995	75.5	117.8	Under
	60	2.5	4	5	6	10	14	26	42	81	960	77.5	125.4	Under
	105	3	5	6.5	9	12	19	31	59	104	910	94.5	205.8	...
	150	3.5	5	8	10	14	21.5	35	68	91	875	75	190.6	...
1-Amidobenzothiazole	60	2	2.5	3	4.5	6	9	14	22	28	870	24	69.5	All cures poor
	90	1.5	2.5	4	5	8	11	18	28	46	880	40	93.6	
	120	2.5	3.5	5	8	10	17	27	50	57	825	47	111.4	
	180	2.5	4	5.5	9	14	23	38	..	54	785	42.5	116.1	
1-Hydroxybenzothiazole	90	0.5	1	1.5	2	3	4	..	..	5	620	3	10.9	No cures
	120	1	2	3	4	4.5	6	9	14	16	840	13.5	42.5	
	150	0.5	1.5	2.5	3.5	4.5	6	10	17	26	880	23	54.2	
	180	1.5	2	3	5	8	10	18	30	38	850	32	79.5	

This mechanism affords an explanation of the following facts:

1—The metallic salts of the mercaptobenzothiazoles are faster curing than the free compounds.

2—Both the metallic salts and the free compounds are faster curing than the disulfides, which must first undergo a reduction to the mercaptans before functioning as accelerators.

3—All mercaptobenzothiazoles require the presence of zinc or lead oxides for the development of full accelerating power.

4—The metallic salt of the mercaptan is therefore assumed to be the active agent. Excess metallic oxide must be present at all times to reform the salt if it should be decomposed by the action of heat or hydrogen sulfide. Evidence of such decomposition is to be found in the low curing power of these salts in the absence of metallic oxides, and their superior power when an excess of the oxide is present.

While it cannot be shown that sulfur split off from polysulfides is an active form, it has been proved that the sulfur in trithio-oxone is particularly active,[6] and it is inferred that the sulfur yielded by the decomposition of the polysulfides is similarly active.

The polysulfide theory, as given above, appears to offer the best explanation of the existing facts. Doubtless, both the mechanisms given above function in specific cases. It is also probable that no simple explanation of activation will be found which is equally applicable to all types of accelerators. Further work is being done to determine the validity of each of the reactions involved in the above mechanisms.

ACKNOWLEDGMENT

The authors wish to acknowledge the coöperation of the Goodyear Tire & Rubber Company as expressed through E. B. Spear, former research director, for the loan of apparatus and the testing of samples. Further acknowledgment is due C. W. Bedford for helpful advice during the early part of the work, W. J. Kelly for valued suggestions, and C. M. Carson for assistance rendered.

Separation of Arsenic and Phosphorus from Vanadium[1]

By H. A. Doerner

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ARSENIC and phosphorus are frequently found in vanadium ores, especially those of the vanadate type, such as vanadinite. Since vanadium ores and intermediate products containing even small amounts of these impurities are not salable, tests were made to establish a commercially feasible method of separation.

It was found that vanadic acid could be precipitated from an acidified vanadate solution containing arsenic and phosphorus. The latter remain in solution and the precipitate may be washed free from these impurities. Further, a vanadate ore containing arsenic and phosphorus may be treated by the method recommended by the Bureau of Mines.[2] The product will be free from these impurities.

EXPERIMENTAL

1—Twenty-six grams of vanadium oxide, 0.85 gram of arsenic trioxide, and 4.38 grams of sodium ammonium phosphate were dissolved in sodium hydroxide solution, oxidized with sodium peroxide, and acidified with sulfuric acid. The solution was diluted to a volume of 1 liter and sulfuric acid was added until the free acid was 0.05 normal in strength as determined by titration with methyl orange. The solution was boiled with live steam for several hours and allowed to stand hot over night. The vanadic acid precipitate was filtered and thoroughly washed. It contained 24.8 grams vanadium pentoxide (95.5 per cent recovery) and not more than a trace of phosphorus or arsenic. The filtrate contained 1.17 grams vanadium pentoxide, and gave a heavy precipitate with magnesia mixture which contained the arsenic and phosphorus.

2—Five hundred grams of a vanadinite concentrate were fused in a graphite crucible with 150 grams of sodium carbonate, 150 grams of caustic soda, and 10 grams of powdered charcoal. The ore analyzed 10.24 per cent vanadium pentoxide, 53.55 per cent lead, 0.28 per cent arsenic, and 0.27 per cent phosphorus. A lead button of 255.0 grams was obtained. The slag was extracted with hot water in a small pebble mill, filtered, and washed. The solution was treated exactly as described in the first experiment except the volume was 2 liters and the separation was completed as before. The residue from, or the undissolved part of, the slag weighed 203 grams, and contained 0.27 vanadium pentoxide, and much of the phosphorus. The net recovery of vanadium pentoxide was 97.2 per cent free from arsenic or phosphorus.

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[1] Received September 19, 1923. Published with permission of the Director, U. S. Bureau of Mines.

[2] "Metallurgical Possibilities of the Descloizite Ores at Goodsprings, Nev.," *Report of Investigations* **2433**.

Poisson's Ratio and Related Properties for Compounded Rubber[1]

By W. W. Vogt and R. D. Evans

The Goodyear Tire & Rubber Co., Akron, Ohio

The structure of compounded rubber, the mechanical relations of the rubber and filler phases, and the effect of these relations upon the physical properties of the compound, furnish the rubber technologist with a most fruitful and stimulating field for speculative reasoning.

The authors have presented new data which indicate that the shape of the filler particles has an effect upon the properties of Poisson's ratio, volume increase under strain, permanent set, and the stress-strain behavior of compounded rubber.

Explanations of the cause of these changes are advanced for the purpose of stimulating thought along these lines, that a deeper and clearer conception of the structure of compounded rubber may result.

IN THE course of some studies on the volume increase of compounded rubber when strained, which studies involved the calculations of the volume from simultaneous readings of length, width, and thickness, it soon became apparent that certain stocks behave decidedly different than others. The point of dissimilarity is that for certain stocks the ratio of thickness to width is a constant, while for others it decreases as the strain increases. This evidence of anisotropy requires that the values for Poisson's ratio in the two directions perpendicular to each other must be unequal.

Furthermore, as the stresses developed perpendicular to each other and to the direction of elongation must, from considerations of the symmetry of forces, be equal, then the fact that different strains are produced by these equal stresses proves that there is a dissimilarity of modulus in the two directions.

Since the various stocks studied differ from each other only in the composition of the filler content, it is evident that the exceptional behavior noted is a function of some property of the filler, and the immediate assumption is that the shape or crystal habit of the particles is the determining factor. It is the purpose of this paper to show the effect of particle shape on the physical behavior of compounded rubber with special reference to the properties of Poisson's ratio, volume increase, set, and the stress-strain relations.

Historical

Whitby[2] gives an admirable resumé and critique of the existing data, and mentions specifically the work of Schiller in which evidence is given to show that the value for P is not the same in different directions.

The "dark Para rubber" sheet used gave values of 0.535 and 0.463 in two directions perpendicular to each other. Schippel[3] calls attention to the fact that the average value for P in the case of a highly compounded barytes stock at the breaking elongation was 0.39. This low value was due to the large increase of volume of the stock, the value presumably having been calculated from density measurements.

The other published data are concerned chiefly with the various methods of determining P experimentally, the proper method of calculation, etc., pure gum stocks having been used almost exclusively.

Experimental Method

Test strips, died out from large sheets, were mounted in a suitable stretching frame, by which any desired elongation could be maintained. The width and thickness were measured, with an accuracy of 0.1 per cent, by a traveling microscope and a gage. It was found necessary to adhere closely to a regular time schedule in performing the several steps of manipulation and observation at each elongation. The shape of the test specimens can be varied over wide limits without affecting the results. The ratio of thickness to width can be varied from 2.5 to 25 without effect, provided the length of the specimens is about twenty times the width. These methods, within the limit of accuracy specified, were entirely satisfactory. As a matter of fact, study of different test pieces cut from the same sheet showed that they differed from each other by such amounts that any higher experimental accuracy would be nonsignificant.

Calculation of Poisson's Ratio

This property is defined as the ratio of the percentage of lateral shrinkage of a rod to the corresponding percentage of longitudinal increase, when such increase is infinitesimally small—that is, if we call L the longitudinal and S the lateral dimension,

$$P = \frac{\frac{dS}{S}}{\frac{dL}{L}} = \frac{dS}{dL}\cdot\frac{L}{S}$$

A graphical method of determining dS/dL was found convenient. The corresponding reading of S and L was plotted and a smooth curve was drawn. The value of the tangent to this curve at each desired point gave directly the value of dS/dL, and hence that of P. This definition of P is to be distinguished carefully from that involving finite changes of S and L. This calculation was applied separately to each of the two lateral dimensions, hereafter spoken of as width and thickness. The following symbols will be used to identify the various values:

P_v = value from volumetric measurements
P_t = value in thickness direction
P_w = value in width direction

It is also possible to calculate an average P_v from the change of volume measurements. If each lateral dimension is considered to have the same value and behavior, the expression for volume becomes

$$V = L\ S^2$$

Differentiating,

$$dV = S^2\ dL + 2SL\ dS$$

$$\frac{dV}{dL} = S^2 - 2SL\cdot\frac{dS}{dL}$$

$$= S^2\left(1 - 2\ \frac{L}{S}\ \frac{dS}{dL}\right)$$

which becomes, from the definition of P,

$$\frac{dV}{dL} = S^2\,(1 - 2P)$$

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[1] Presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] "Plantation Rubber and the Testing of Rubber," p. 486.

[3] This Journal, **12**, 33 (1920).

Hence,

$$P = 1/2\left(1 - \frac{1}{S^2}\frac{dV}{dL}\right)$$

If, further, at each desired elongation, V, L, and S are measured in such units that their instantaneous values are each unity, this becomes

$$P = 1/2\left(1 - \frac{dV}{dL}\right)$$

By plotting V against L, this average P can be computed, using the graphical method for determining dV/dL mentioned above.

The values of P_v calculated by this method were in excellent agreement with the arithmetical average of P_t and P_w as required by the principles of mechanics.

Experimental Data

The results show that the common compounding ingredients may be divided into two classes—those which the writers call "anisotropic," which cause anisotropy of properties in the stocks in which they are compounded, such as graphite, mica, tripoli, clay, light magnesium carbonate, and, strangely enough, glue. The other class, which the writers have called "isotropic pigments," do not exhibit these tendencies, and include gas black, lampblack, iron oxide, zinc oxide, lithopone, and barytes.

Thickness-Width Ratio—The first criterion which was used in classing the pigments was called the thickness-width ratio. If the reading of thickness is divided by the corresponding reading of width as the test pieces are progressively strained, the values obtained constantly decrease for the anisotropic fillers, and remain constant for the isotropic class. The writers have recalculated all values of T/W in such a manner that the value T/W at 0 per cent elongation becomes 1.0.

The data shown in Fig. 1 were obtained on stocks containing 20 volumes of filler per 100 volumes of rubber, cured to the correct technical cure.

The stocks were milled on small (6 × 12 inches) rolls in such a manner as to "set the grain"—i. e., align the pigment particles—were allowed to age 1 hour on a warming table to permit readjustment of internal strains in the rubber phase, and then 24 hours at room temperature, after which they were cured in molds, using enough stock to give a perfect sheet with a small overflow (5 per cent). Unless otherwise noted, all test pieces were died out in the direction of the grain.

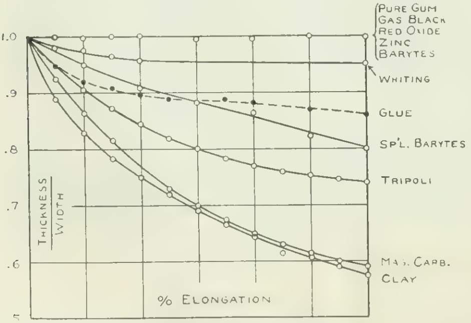

Fig. 1

Poisson's Ratio—The T/W ratio is a criterion which is easily obtained experimentally and can be calculated and interpreted readily. However, Poisson's ratio is a recognized absolute property, and was therefore specifically calculated in all cases.

In considering the value of Poisson's ratio, the following cases must be considered:

When the volume of the rubber under strain remains constant, we have two cases:

(1) $P_w = P_t = 0.5$

(2) P_w does not equal P_t, but $\frac{P_w + P_t}{2} = 0.5$

When the volume does not remain constant on stretching, we may have

(3) $P_w = P_t < 0.5$

(4) P_w does not equal P_t, and $\frac{P_w + P_t}{2} < 0.5$

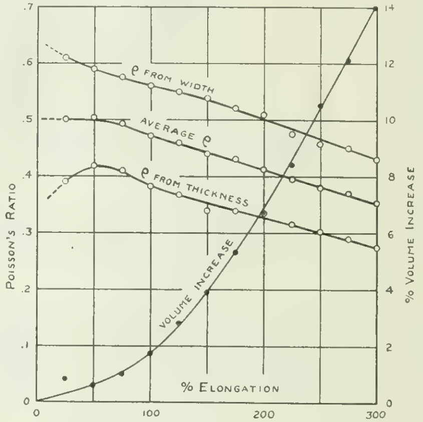

Fig. 2

Case 1—All isotropic pigments studied fulfil Case 1 at low elongations (25 per cent), because the volume changes are practically negligible. Such fillers as gas black and zinc oxide fulfil the conditions up to elongations of 200 per cent, there being practically no increase of volume at this elongation. The values for P_t and P_w are both 0.5.

Case 2—The values for P_t and P_w for some typical anisotropic pigments at 25 per cent elongation are given in the following table:

Table I

Pigment	P_t	P_w	$\frac{P_t + P_w}{2}$
Magnesium carbonate	0.72	0.30	0.51
Clay	0.69	0.32	0.505
Tripoli	0.61	0.39	0.50
Special barytes	0.57	0.42	0.50

Case 3—This case is illustrated by barytes, lithopone, and other isotropic pigments at high elongations, say 300 per cent, where there is a considerable increase in volume.

Case 4—This is illustrated very neatly by tripoli, an anisotropic filler which gives large volume increases at high elongations. This behavior is represented graphically in Fig. 2. The volume increase curve is also given.

It will be readily appreciated that for low elongations the graph shows the behavior as given under Case 2, while for the higher elongations the conditions fulfil Case 4.

Stress-Strain Relations in Different Directions—As had been stated above, stocks compounded with anisotropic pigments should give different stress-strain relations in different directions. Therefore, a stock containing 20 volumes of clay per 100 volumes of rubber was so prepared that stress-strain curves might be obtained, the tests being taken with the grain, across the grain, and vertical to the grain (perpendicular to the plane of the calender). The preparation of the last-mentioned test piece is rather difficult, the alignment of filler particles probably being quite badly disarranged during the process. However, the tests were obtained, particular care being exercised to secure identical curing conditions. The results are shown graphically in Fig. 3.

Additional properties of these three stocks were determined as follows:

TABLE II

	Volume Increase at 250%	T/W at 250% Elongation	Permanent Set
	%	%	
With grain..	4.4	0.76	44
Across grain.	5.5	0.69	36
Vertical to grain	8.1	0.74	[illegible]

PERMANENT SET

Values for permanent set for stocks compounded with 20 volumes of filler per 100 volumes of rubber are given in the following table:

TABLE III

	PIGMENT	PERMANENT SET %
ANISOTROPIC FILLERS	Magnesium carbonate	52
	Clay	44
	Special barytes	32
	Tripoli	29
ISOTROPIC FILLERS	Gas black	33
	Zinc oxide	23
	Red oxide	22
	Lithopone	20
	Whiting	15
	Barytes	14
	Pure gum	6

A comparison of the properties of ordinary and the special barytes brings out strikingly that particle shape, rather than such factors as degree of fineness, surface activity, selective wetting, or adsorption, is the fundamental cause of these abnormal properties. The special barytes was made by such a process that it consists almost entirely of long, flat plates and needles, whereas the regular barytes was the commercial ground product, consisting of broken fragments of no regular geometric shape. The samples were closely alike as regards average particle size and were compounded on the basis of 20 volumes of pigment per 100 volumes of rubber. The values for *T/W* ratio, Poisson's ratio, and permanent set are given below.

TABLE IV

	T/W Ratio at 200% Elongation	P_t	P_w	$\frac{P_t + P_w}{2}$	Permanent Set %
Regular barytes.........	1.00	0.50	0.50	0.50	14
Special barytes..........	0.86	0.57	0.42	0.50	32

The stress-strain relationships (taken with the grain at the correct technical cure) furnish additional evidence of differences between the isotropic and anisotropic fillers.

TABLE V

	100%	300%	500%	Tensile Kg./Sq. Cm.	Elongation %
Regular barytes.......	7	17	42	132	700
Special barytes........	18	42	91	160	640

The four properties mentioned above are dependent to a greater or less degree upon crystal habit, but it is believed that Poisson's ratio and the *T/W* ratio are almost wholly dependent on this characteristic.

LAMINATION EFFECTS OF THE CURED STOCK

The ability to separate the cured sheet into layers in the same manner as a sheet of mica may be split is another criterion which may be used to demonstrate anisotropy. The pigments that give stocks which laminate are mica, graphite, clay, magnesium carbonate, tripoli, and the special barytes. Here again the differences between the special and regular barytes are especially striking. It will be recognized that these fillers are without exception classed as anisotropic by other methods.

VEILS

The familiar silky appearance of the precipitate which forms on adding mercuric chloride to a solution of stannous chloride, or that due to a suspension of bismuth subnitrate or vanadium pentoxide in water, has been directly proved to be caused by the needle or tabular shape of the solid particles, and Freundlich[4] has developed a method for determining crystal habit based upon the changes in the strength of the Tyndall beam, depending upon the plane of observation with respect to the alignment of the particles. The presence of this "veil" (German word is "Schlierenbildung," meaning veil formation) is a qualitative test for anisotropy of shape.

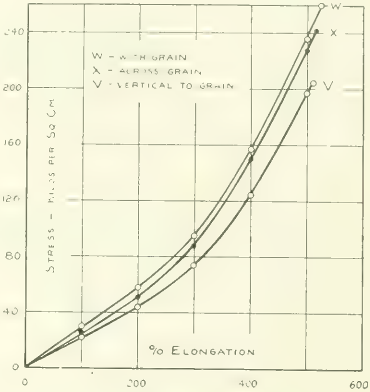

FIG. 3

If a dilute suspension of the pigment is made in water, preferably with gum arabic as a protective colloid, agitation of the suspension will reveal the presence of veils only in the case of anisotropic pigments. Mica furnishes a very excellent example of this effect. The size of the particles of pigment will probably have some influence upon the phenomenon, so it would not be absolutely proved that a pigment which does not show the effect is isotropic. However, all the pigments which by other means have been classed as anisotropic give veils, whereas none of the isotropic pigments give the effect.

The differences between the special and regular barytes, which have been noted by the other methods, are strikingly revealed by this test.

DISCUSSION OF RESULTS

The experimental results given above were obtained on stocks which were so prepared as to suppress the grain effects due to the rubber phase and to accentuate the effects due to the filler phase so far as this is possible. With this point clearly in mind, the evidence is positive that the shape of the filler is a major contributing cause of the changes in the properties of the stocks. The questions to be answered therefore are:

1—What shape is necessary to explain these effects?

2—What is the mechanism of the action by which these effects are produced?

In view of the known facts that the particle shape of mica, graphite, special barytes is tablets or placques, and that tripoli contains a large percentage of tabular diatoms, the writers are justified in saying that any shape wherein any two dimensions are considerably greater than the third will explain the effects observed.

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[4] *Physik. Z.*, **17**, 117 (1916).

In answer to the second question as to the mechanism, the following reasoning is advanced in explanation of the facts. The following conditions are postulated:

1—There is a union between the particles of filler and the rubber, which bond may be chemical union, physical adsorption, surface friction, or mechanical interlocking. An estimation of the magnitude of these forces is unnecessary.

2—The particles of filler are uniformly distributed throughout the rubber, this uniform distribution thereby necessitating that on the average the centers of mass of the particles be approximately equidistant.

3—In the normal milling or calendering operations, the particles of an anisotropic pigment tend to align themselves with their longest axis in the direction of the calender, and with their least dimension perpendicular to the plane of the calender.

With these conditions in mind it will be obvious that in the direction of the calender grain the edges of the crystals will be closer together than in the direction at right angles to the direction of the calender, which in turn will be closer than those in the direction perpendicular to the plane of the calender. In other words, in a given linear distance, the sum of the lengths of the filler particles will be greatest with the grain, intermediate across the grain, and least vertical to the grain. Conversely, the amount of rubber phase between the filler particles will be least, intermediate, and greatest with the grain, across the grain, and vertical to the grain, respectively.

Consequently, to effect a given elongation in any direction, inasmuch as the pigment phase does not elongate, the rubber must be stretched to such a point as will give the total elongation desired. It is therefore evident that the lesser amount of rubber will have to be elongated to a greater proportion of its ultimate elongation. This means that a higher stress must be imposed. This, then, is the reason why a stock compounded with an anisotropic filler has a stiffer stress-strain curve with the grain. The stress-strain across the grain may be equal to or softer than the "with grain" curve (depending on the ratio of the length to width dimensions of the particular filler), but both will be stiffer than the "vertical to grain" curve.

Referring to the values of permanent set given in Table III, it is found that, within each class of pigments, the permanent set is greater the smaller the particle size. That is, permanent set increases with increase of filler surface, and this fact lends weight to the argument that permanent set is in part due to a dislodgment of rubber and pigment surfaces, which, having been cured up in contact with each other, on removal of the stretching force experience frictional difficulty or even definite obstruction in becoming readjusted to their original condition of fit. Since anisotropic particles have more surface per unit volume than isotropic particles of the same average bulk, for this reason alone they might be expected to show greater permanent set.

Furthermore, for anisotropic pigments the greatest amount of rubber-pigment interface will be involved in this dislocation under strain when that strain is parallel to the longest dimension of the pigment—that is, with the grain—intermediate in value when the strain is across the grain, and least when the strain is vertical to the grain. Hence, we should expect the permanent set for the stocks referred to in Table II to be greatest for the "with grain" stock, intermediate for the "across grain" stock, and least for the "vertical to grain" stock. Permanent-set measurements on these three stocks gave, respectively, 44, 36, and 30 per cent.

Mention is made above of the volume increases which occur when the stock is subjected to strain in the three different directions. Schippel has shown that the per cent increase in volume is largely a direct function of the area of the particle in a plane normal to the strain lines. The areas so defined and therefore the values of volume increase, in the case of these clay stocks, will be least, intermediate, and greatest, for strains in a direction with the grain, across the grain, and vertical to the grain, respectively. The values found were 4.4, 5.5, and 8.1 per cent.

The T/W ratios obtained when the direction of strain is always parallel to the length of the test piece, but where the length of the test piece itself is with the grain, across the grain or vertical to the grain, furnish a fascinating subject for speculative analysis.

By an extension of the reasoning used in developing the explanation for the difference in stress-strain behavior, in a qualitative way, at least, the causes for the variation in T/W ratios in different directions can be explained.

Thus, when a strain is imposed parallel to the grain, considerations of symmetry require that the contractive stresses in the two lateral directions must be equal. Since, however, as has been outlined above, the percentages of rubber phase in a given linear distance are unequal in the widthwise and thickwise dimensions, the imposition of equal stresses will cause equal strains to be set up in the rubber phase but unequal total contractions of the material as a whole, since the pigment phase is rigid.

The exact quantitative differences in the T/W ratio in different directions depend on relative magnitudes of the average ratios of each pair of dimensions of the pigment particles, assuming that the particles are perfectly uniform in shape, size, distribution, and orientation, a condition which is well-nigh experimentally impossible.

The T/W ratios given in Table IV are explainable on the basis that the length, width, and thickness dimensions of the typical clay particle are approximately as 5 : 2 : 1.

The explanation of the lamination effects observed with typical anisotropic fillers probably is that the bond between the filler surface and the rubber is less than the tensile of the rubber itself. Therefore, instead of the rubber tearing within itself in a haphazard, irregular direction, it separates from the broad faces of the filler particles. The line of cleavage is thus defined by the alignment of the filler particles and lamination ensues.

These explanations of the experimental facts justify the hypothesis advanced and may possibly give a clearer conception of the structure of compounded rubber and of the effect of the filler phase upon some of the properties of this material with particular reference to its anisotropy.

M. Carey Lea—Chemist

America's contributions to chemistry have been the theme of years of study by Edgar F. Smith, and through the publication of these studies he has done more than any other one man to put the facts of these discoveries and discoverers before American chemists. The latest work from his kindly pen is entitled "M. Carey Lea—Chemist."

Lea (1823–1897) was a student under J. C. Booth in his famous teaching laboratory, after having studied law and having been admitted to the bar. His studies after leaving Dr. Booth's laboratory were largely carried out in his private laboratory in his home in Philadelphia. His most important investigations dealt with picric acid and the picrates, the Pennsylvania coal seams, the metals of the platinum group, and photography. His work on photography was decidedly his most important contribution to knowledge. His only book, "Photography," went through two editions and was extremely popular with the devotees of this new art at the time. Lea was a recluse and was known personally to few of his contemporaries. His work was published in the *American Journal of Science* from 1858 to 1897, and *Chemical News*, 1862, contains four contributions from his laboratory.

The present story of his life is published privately by the author in a 12-page pamphlet with an engraving of the subject.

Selenium in Rubber Compounding[1]

By Ira Williams

Firestone Tire & Rubber Co., Akron, Ohio

Selenium may be introduced into rubber by the addition of fused mixtures of sulfur and selenium. The color produced changes from yellow to red as the size of the particles of selenium increases.

The crystallization of sulfur in rubber may be induced with selenium because selenium is isomorphous with monoclinic sulfur. In this way metastable solutions of sulfur are prevented and the initial rapid bloom of uncured stocks may be eliminated.

Selenium exerts a distinct accelerating action upon rubber-sulfur mixtures, while the actual amount of combination with selenium is small.

Selenium alone will produce some cure in rubber in the presence of an organic accelerator.

The acetone extract of resin from the rubber is apparently reduced when vulcanization is carried out in the presence of selenium.

It is to be expected from the chemical analogy between oxygen, sulfur, selenium, and tellurium, that any of these would produce vulcanization in a rubber compound. Probably the most important of these, other than sulfur, is selenium, and it has been shown by Boggs[2] that selenium may be used as a vulcanizing agent. It is possible that the effectiveness of these materials in the vulcanization process will depend somewhat on the effective concentration of the material in the rubber. While sulfur is quite soluble in rubber, tellurium is insoluble. The best figures which have been obtained in the present work place the solubility of selenium at less than 0.05 per cent at 80° C. Oxygen is somewhat more soluble, and it is known that cures may be obtained by means of oxygen without the presence of sulfur. In the case of sulfur the effective concentration may be very much increased at temperatures above its melting point, but in the case of both selenium and tellurium it is impossible to reach their melting points (217° and 451° C., respectively) without producing decomposition in the rubber. If the effectiveness of these elements in producing vulcanization of rubber is judged by the possible molar concentration, the elements would then be placed in the order—sulfur, oxygen, selenium, tellurium. This order might be affected if a higher concentration could be produced by such means as introducing the element in an adsorbed condition or in a finer state of division.

Sulfur and selenium are miscible in the fused state in all proportions, and form a eutectic mixture which melts at 106° C. and contains 40 atomic per cent of sulfur. Mixtures of this kind crystallize very slowly, and immediately after fusion may be milled into rubber to form a master batch which will keep for an indefinite period. In this manner mixtures of sulfur and selenium containing as high as 70 per cent of selenium may be prepared and held in rubber for use in compounding. While selenium may be used without first fusing with sulfur, the equilibrium of the system will be reached quite slowly, especially at low temperatures, and the same distribution of selenium cannot be obtained.

Color in Selenium Stocks

The colors obtained by introducing a fused mixture of sulfur and selenium into rubber are produced by the distribution of sulfur between the rubber and selenium. In this manner colloidal selenium is formed. The uncured stock varies from a bright yellow, when little selenium is present in a very fine colloidal state, to a deep orange color when more selenium is used. Upon curing, the size of the colloidal particle slowly increases and the color changes from yellow through orange, deep red, brown, and finally to the natural color of cured rubber. By regulating the time of cure and the amount of selenium, any of these colors may be produced in the finished stock and will be quite permanent at ordinary temperatures. By the time the color of the stock has reached red, particles of selenium may be seen under the microscope, while if the cure is continued the selenium will finally gather into spherical crystals which can be seen with the unaided eye.

Crystallization Phenomena

It is a common observation that compounds of low sulfur content bloom very easily while in the uncured state. This is due to the fact that the temperature reached during the milling period is sufficient to cause all the sulfur to go into solution. Upon cooling, the system becomes metastable because the rubber is supersaturated with sulfur. When the surface of such a stock is touched, crystallization occurs at that point, and these crystals serve as nuclei for the growth of the large crystals which quickly appear as bloom.

Metallic selenium, because of its being isomorphous with monoclinic sulfur, may be used to prevent the formation of a supersaturated solution of sulfur. If 0.05 or 0.10 per cent of finely divided selenium is milled into the stock, each particle of selenium, which owing to its low solubility and the slow rate at which equilibrium is established at low temperatures, becomes a center for the crystallization of sulfur. After crystallization has taken place a disturbance will not produce bloom, and the condition known in the industry as "dry stock" may in this way be quite effectively avoided. In a pure gum stock this crystallization requires from 10 to 15 minutes, but since crystallization is slower in the presence of a large volume of filler, it is necessary to produce more centers of crystallization by using a larger quantity of selenium.

Experimental

As a control for a study of the effect of selenium on cure, a simple rubber-sulfur mixture was used. Replacement of part of the sulfur by selenium was done on a molecular basis. In each of the following compounds the sum of sulfur and selenium is equivalent to 6 per cent of sulfur to the rubber.

Stock	Pale Crepe G.	Sulfur G.	Selenium G.
47	94.00	6.00	0.00
48	94.00	5.11	2.19
49	94.00	4.51	3.69
50	94.00	3.73	5.60
51	94.00	0.00	14.80

These stocks were cured at 290° F. in an oil bath which controlled the temperature to ± 0.5° C. The physical properties of all, with the exception of Stock 51, which showed no signs of cure after 5 hours, are plotted in Fig. 1. In such a diagram the rate of cure (not to be confused with time of "optimum" cure), as measured by the rate of change in stiffness of the stock, can be judged by the slope of the first part of the curve. The addition of selenium has produced an increased rate of cure in all compounds containing sulfur. Stock 48, which contains only 2.17 per cent of selenium, cures at approximately twice the rate of the simple rubber-sulfur mixture. After this the addition of selenium at the expense of sulfur causes a decrease in the rate of cure until finally a stock which does not cure at all results.

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[1] Presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] This Journal, **10**, 117 (1918).

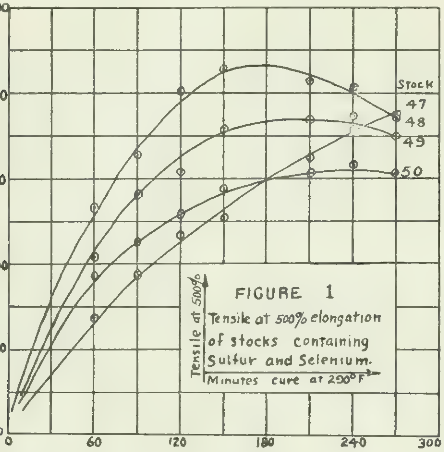


FIGURE 1
Tensile at 500% elongation of stocks containing Sulfur and Selenium.

There are at least two possible factors which influence the rate of cure of these stocks.

(1) The solubility of the selenium may be increased until it becomes an effective vulcanizing agent.
(2) The selenium may act simply as an accelerator.

The mixture of sulfur and selenium having the lowest melting point contains 62 per cent by weight of selenium. Stock 48, which shows the highest rate of cure, contains only 30 per cent by weight of selenium in the sulfur-selenium mixture, but since the selenium is very slightly soluble in the rubber, the distribution of sulfur between the rubber and the selenium may be such that the eutectic mixture of sulfur and selenium is approached. Further addition of selenium and reduction of sulfur would then result in a higher melting point and reduced vulcanizing properties. This is probably true if selenium functions in the same manner as sulfur, but does not necessarily follow if the selenium acts merely as an accelerator. That selenium does act as an accelerator is indicated by the curves in Fig. 1, since the addition of only a small amount of selenium has greatly increased the rate of cure, while the selenium alone produced no cure. After the addition of selenium the decrease in sulfur has retarded cure in a manner similar to that experienced when the sulfur is reduced in the presence of an organic accelerator. The accelerating action (in per cent) is shown further by the following stocks, in which a small amount of selenium has been added to a compound already containing an organic accelerator:

Stock	Rubber	Sulfur	Zinc Oxide	Aldehyde Ammonia	Selenium
52	93.00	3.00	3.00	1.00	0.00
53	92.80	3.00	3.00	1.00	0.20

The physical properties of these compounds are shown in Fig. 2. Both the rate of cure and stiffness of the rubber have been increased much more than they would have been by the addition of either the same amount of aldehyde ammonia or sulfur. This indicates either a marked activity as an accelerator or a specific action of selenium which is produced by neither accelerator nor sulfur.

Neither of these explanations is in itself sufficient to explain the action of selenium, because, as pointed out by Boggs, selenium is capable of producing a cure at the temperature employed if an organic accelerator is added. A stock containing 70 per cent of rubber and 30 per cent of selenium showed no cure after 5 hours at 290° F. The same stock with 2 per cent of rubber replaced by 1 per cent of zinc oxide and 1 per cent of aldehyde ammonia gave a tensile of 1300 pounds after 30 minutes' cure. The stiffness and strength slowly decreased upon longer cures until it reached a tensile of only 900 pounds after 4 hours. This behavior is distinctly different from that of a rubber mix containing such a high percentage of sulfur, in which case the stiffness would have continued to increase.

Analysis of Stocks Containing Selenium

The determination of the chemical properties is accomplished with difficulty because of the presence of both selenium and sulfur. It is possible by means of an ordinary acetone extraction to remove some selenium. Bloom which occurs on undercured sulfur-selenium stocks is composed of both sulfur and selenium, so that the mixed crystals of sulfur and selenium are somewhat soluble in rubber and may be extracted. Further extraction of selenium after the free sulfur has been removed is extremely slow. The extraction is made all the more difficult by the fact that selenium, which is heated even to temperatures as low as 100° C., tends to assume the more insoluble form. It is possible that repeated addition of sulfur to the stock with repeated extractions might be a means of removing all free selenium. Crystals were found in Stock 48 after curing for 60, 90, or 120 minutes. Small strips, each 0.02 inch in thickness, were placed in a Soxhlet apparatus and extracted with acetone. Although the 60-minute cure contained the most crystals, all had disappeared after 2 hours of extraction. Those in the 90-minute cure had practically disappeared after 6 hours, while the 120-minute cure had apparently not changed after 2 days. A microscopic examination revealed the fact that, while the crystals were once well formed, they had been reduced during the

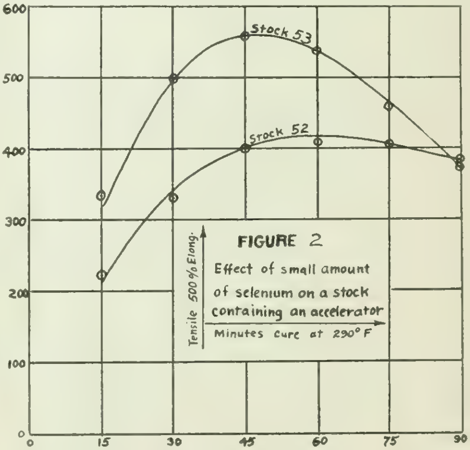
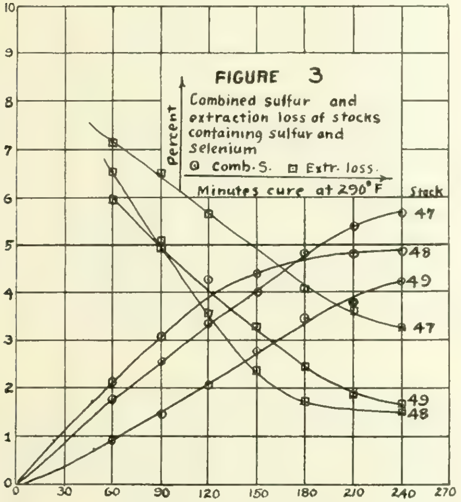


FIGURE 2
Effect of small amount of selenium on a stock containing an accelerator

extraction to a series of broken points which, without magnification, still showed the original outline. These changes again point to the fact that free sulfur is necessary for the successful extraction of selenium.

Microscopic examination was made of sections of sulfur-selenium stocks which were cured to the point where practically no free sulfur remained. The amount of selenium present was estimated by counting and measuring the particles, and, within the limits of accuracy of this method, all the selenium could be accounted for. This showed that the amount of combined selenium must be small and is not to be compared in magnitude with the amount of combined sulfur. No further efforts were made to determine combined selenium.



Mixtures of sulfuric and selenic acid may be separated in acid solution by the addition of potassium iodide. The iodine may then be titrated with standard arsenite and the selenium determined, after which the sulfate may be precipitated. This method cannot be used if a nitrate fusion has been used in the oxidation of the sulfur and selenium, unless the nitrate and nitrites are first removed. If the selenium is not to be determined it may be reduced in the presence of a nitrate, but the presence of nitrites, which are always produced during the fusion, prevents the precipitation of selenium. This precipitation is, however, easily accomplished in acid solution by either sulfites or stannous chloride. Combined sulfur was finally determined after removal of selenium by the addition of the calculated amount of stannous chloride. The following check determinations were made by this method on a stock of known sulfur and selenium content:

Sulfur Present G.	Selenium Present G.	Sulfur Found G.
0.0163	0.0103	0.0162
0.0163	0.0103	0.0159
0.0163	0.0103	0.0167
0.0163	0.0103	0.0169

In Fig. 3 are shown the values for combined sulfur and for extraction loss of Stocks 47, 48, and 49. In all stocks containing selenium, the same stiffness is reached with lower combined sulfur. This resembles the action of stocks containing an organic accelerator. The extraction loss of the rubber-sulfur mixture reaches a minimum of 3.3 per cent at 240 minutes' cure. This is slightly more than the normal resin content of the rubber. In all the selenium stocks a minimum extract of only slightly more than 1.5 per cent is found. This is approximately 1.1 per cent below the original resin content of the rubber.

Although selenium alone or with an accelerator is somewhat effective as a vulcanizing agent, it is apparent that it functions chiefly as an accelerator when used with sulfur. All accelerators in common use, whether organic or inorganic, are chemical compounds, but here is a case of the increased action being brought about by an element. Complications arising in the study of the accelerators of vulcanization can be greatly reduced by the elimination of many uncertain decomposition products, if selenium is used as the accelerator. The action between accelerator and sulfur is also reduced to a more simple state. It is possible that a study of the action of selenium in rubber will throw more light on the nature of acceleration.

A Ball-Mill Electrolytic Cell[1]

By Alexander Lowy and Alfred R. Ebberts

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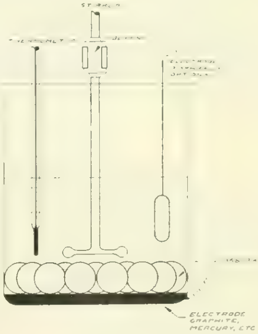
During the course of an investigation in this laboratory of the electrolytic oxidation of anthracene, a novel type of cell was designed and constructed. Certain solids in suspension have a tendency to aggregate under the action of the current. Also, when the superficial layer of any particle has entered into reaction, it prevents or slows up the action on the central portion of the particle. To prevent both of these undesirable effects this cell was designed.

The stirrer was equipped with paddles to produce a swirling motion in the electrolyte, and glass balls were introduced, which were carried rapidly round and round by the swirling liquid. The thermometer and one electrode were raised enough to allow the balls to pass under them. The other electrode was on the bottom of the beaker and a connection for it was sealed in the glass. For large balls several glass marbles, such as children play with, were used, and for small ones the solid beads furnished for Hempel fractionating columns. The size of ball must be determined by conditions. Mercury as electrode has the advantage of not requiring sealing into the cell, and also that no trouble due to solids adhering to the electrode surface is experienced. The solid anodes used by the authors were sealed in place with Redmanol cement, which was found to be very satisfactory. Heat should be supplied by bath only. Direct heating causes the dissolution of the cell due to the different coefficients of expansion of the materials used and the excessive local heating.



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[1] Received September 13, 1923.

Some of the Constituents of Coke-Oven Tar[1]

By John M. Weiss and Charles R. Downs

50 East 41st St., New York, N. Y.

THERE is a rather popular idea that anything can be found in coal tar, based on the assumption of the layman that coal-tar products are in general found in tar itself. Even the technical man is under some misapprehension, as Lunge in his book on "Coal Tar and Ammonia" lists some two hundred odd substances which various investigators have claimed to have found in tars from various sources, including such widely differing types as blast furnace, peat, lignite, and wood tars, as well as the various tars from bituminous coal. The type of tar produced in greatest quantity in the United States is coke-oven tar, so it seems that more exact information on its composition is desirable. The past exact knowledge is largely confined to the light oil below 200° C., the tar acids, and the tar bases, all of which are comparatively easy to separate and examine.

The present communication is designed to throw light on the composition of the neutral oils boiling above 200° C., both as to the principal compounds present and their amount. Naturally, a study of the composition of all varieties of American coke-oven tars would be a very long investigation, but the composition of the average coke-oven tar is of interest to show what compounds are commercially available. The results can be accepted with the usual reservations which all conversant with the tar industry make because of the variations in the raw material of the industry. The work described comprises two phases—qualitative and quantitative.

The qualitative test involved a larger sample than chemists are wont to use in their analyses. About 20,000 gallons of coal-tar distillate oil were handled, the tar acids and bases removed by extraction with caustic soda solution and dilute sulfuric acid, and the extracted oil was settled to remove the hydrocarbons crystallizable at normal temperature. This left about 10,000 gallons of neutral settled oil, which was distilled in the most refined type of vacuum column still. The distillate was collected in 100-gallon fractions, and these fractions were taken for the laboratory qualitative examination, first, to determine the existing compounds, and, second, to develop quantitative methods for estimation of these compounds. In this paper the detailed results of the preliminary experiments are not given in full, but rather a skeleton of this phase of the work and the final general conclusions reached.

METHYLNAPHTHALENE

The separation of α- and β-methylnaphthalenes was undertaken from the fractions of oil boiling between 235° and 247° C. After a number of fractional distillations and crystallizations, fairly pure samples of the two isomers were obtained. The β-methylnaphthalene was crystallized fourteen times from alcohol and finally showed a solidifying point of 35.1° C. and an index of refraction at 40° C. of 1.6028. The melting points of successive crops of crystals had not become absolutely constant, but were nearly so.

The α-methylnaphthalene was purified by recrystallizing the picrate and decomposing it. The melting point of the picrate was 123° C. and the index of refraction of the hydrocarbon at 40° C. was 1.5882. There was therefore sufficient difference in the indices of refraction to use this constant as a method of estimation, if only the two isomers were present in a mixture. The constant is seriously depressed by the presence of paraffins in the oils which may amount to 4 per cent. All other impurities, however, can be removed and the paraffins estimated and their effect on the index of refraction calculated from the determined value for their index of refraction at 40° C. of about 1.4316. The writers did not go further into the properties of the monomethylnaphthalenes, as at this point they had sufficient data to enable them to make reasonably approximate estimates of the methylnaphthalene content of oils, and had concluded, further, that in general, with the products investigated, the proportions of α- to β-methylnaphthalene were 1.45 to 1.00.

The fractions containing the methylnaphthalenes were examined for trimethylcoumarones, with negative results. The fractions just above the monomethylnaphthalenes contained dimethylnaphthalenes in complex mixture. No attempt was made to separate the individual isomers, but they were estimated *en masse* by fractional distillation.

DIPHENYL

This body was estimated in several of the fractions by sulfonation at 40° to 50° C. with concentrated sulfuric acid and pouring the sulfonated mass into an excess of water. By extraction with ether, a crude diphenyl was obtained which was purified from admixed paraffin hydrocarbons by crystallization from alcohol. The richest fraction contained only 8 per cent of the crude material, and, based on the original tar, the amounts present were only around 0.1 per cent.

FLUORENE

The fractions in which fluorene should be present were nearly solid and the separated pressed solids were nearly pure material, merely requiring a wash with sulfuric acid and redistillation to remove small amounts of resinifying hydrocarbons.

ACENAPHTHENE

The fractions in this range acted very similarly to the fluorene fractions, and the isolation of acenaphthene was not difficult. The separated liquid oil from acenaphthene, as well as that from fluorene, was not examined very thoroughly, as on redistillation it gave considerably more of the parent hydrocarbon and the actual amounts of true liquid oil were materially lessened.

PHENANTHRENE

The development of a direct method of analysis for phenanthrene in crude solids was a long and tedious task. The method finally perfected involved the formation of phenanthraquinone by oxidation in glacial acetic acid solution with iodic acid and the precipitation of the phenanthraquinone in weighable form by either 1,3,4-toluylenediamine or 1-ethoxy-3,4-diaminobenzene. The details of this form the subject of a paper by Williams.[2] In connection with the work pure phenanthrene was prepared and found to have a melting point of 99.6° C.

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[1] Presented before the Division of Organic Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *J. Am. Chem. Soc.*, **43**, 1911 (1921).

Miscellaneous

Naphthalene, anthracene, and carbazol were separated and estimated in the usual way in the solids from their fractions. Diphenylene oxide was sought, with negative results. Above the anthracene oils are obtained the last oils from the distillation of tar which can be roughly separated into yellow solids, greases, and resinous bodies—all of unknown composition and affording fields for further research work. The separation of these products has been described by Bailey and Boettner.[3] The yellow solids have been shown to contain chrysene and picene, and are a rather complicated mixture.

As exemplifying the work, the results obtained on one of the still runs of higher boiling oil are shown graphically in the accompanying curve. Still temperatures are not given, as under a varying vacuum they are of very little value. In the greater portion of the range over 70 per cent of the compounds present were actually definitely determined. The percentages of acenaphthene and fluorene as determined are probably somewhat low and account partly for the drop of the total curve between Fractions 16 and 23. The fractions also vary in paraffin content from 2 to 5 per cent and from 5 to 7 per cent in unsaturated hydrocarbons, but as these have not been determined in all fractions in this set, they were omitted. If included they would bring a considerable portion of the total curve close to 100 per cent. The naphthalene and monomethylnaphthalene end is not characteristic as these had been largely removed by a previous distillation.

Constituents of Tar

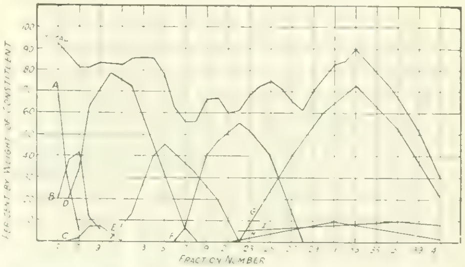
With the data obtained in the preliminary work a new start was made. A mixture of four representative coke-oven tars with a specific gravity at 15.5° C. of 1.186 and a benzene insoluble of 10.6 per cent was selected, and was run first in the plant and then in the laboratory, distillation losses being eliminated by equation as the work proceeded. The net final results are shown in the following table:

Constituents of Tar

	Per cent by Weight on Dry Tar
Light oil:	
Crude benzene and toluene	0.3
Coumarone, indene, etc.	0.6
Xylenes, cumenes, and isomers	1.1
Middle and heavy oils:	
Naphthalene	10.9
Unidentified oils in range of naphthalene and methylnaphthalenes	1.7
α-Monomethylnaphthalene	1.0
β-Monomethylnaphthalene	1.5
Dimethylnaphthalenes	3.4
Acenaphthene	1.4
Unidentified oil in range of acenaphthene	1.0
Fluorene	1.6
Unidentified oil in range of fluorene	1.2
Anthracene oil:	
Phenanthrene	4.0
Anthracene	1.1
Carbazol and kindred nonbasic nitrogen-containing bodies	2.3
Unidentified oils, anthracene range	5.4
Phenol	0.7
Phenol homologs (largely cresols and xylenols)	1.5
Tar bases (mostly pyridine, picolines, lutidines, quinolines, and acridine)	2.3
Yellow solids of pitch oils	0.6
Pitch greases	6.4
Resinous bodies	5.3
Pitch (460° F. melting point)	44.7
Total	100.0

The general composition of the distillate portion of the tar is fairly well accounted for, the unidentified material in the lower ranges being inconsiderable (largely unsaturated hydrocarbons and paraffins or hydro-aromatics), the greater part of the unidentified materials occurring in the oils of the anthracene range and the solids and greases just below the hard pitch.

It is, of course, to be borne in mind that these results represent the composition of a mixture of several coke-oven tars, and other mixtures or single varieties of these might show different percentages of materials, but these variations cannot be estimated at present. The amounts given should not be taken as commercially recoverable, as it would not ordinarily be practicable to refine oils to the extent necessary to obtain all of any given constituent.



A—Naphthalene B—Monomethylnaphthalenes. C—Diphenyl. D—Dimethylnaphthalenes E—Acenaphthene F—Fluorene G—Phenanthrene H—Anthracene I—Carbazol

The most notable feature of the results is the comparatively few compounds existing in the tar in appreciable amount, probably not over one-quarter of those popularly supposed to be there. The fact that phenanthrene is the second most abundant chemical in tar is also surprising and indicates the desirability of work to effect its chemical utilization. The higher boiling resins and greases are worthy of attention by future chemical investigators, as they are present in considerable quantity, and further amounts of the resins are left in the 460° F. melting point pitch, although this (containing from 50 to 60 per cent of free carbon and considerably harder than ordinary commercial pitches) is very close to pitch coke. The method of tar distillation was such as to minimize cracking, as shown by the fact that the 460° F. pitch was entirely fluid when drawn from the still.

The writers believe that the results given are new and afford a better picture of the constituents of American coke-oven tar than has heretofore been available. They may serve to correct many misconceptions which have been prevalent in the past, and should indicate certain fields in which effort toward the isolation and utilization of coal-tar products is desirable.

A New Ethylating Agent

For some time the Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa., in connection with the work of the Multiple Industrial Fellowship sustained by the Carbide & Carbon Chemicals Corp., of New York City, has been making a thorough investigation of the properties and uses of diethyl sulfate as a general ethylating agent. A. R. Cade, an industrial fellow of the institute, under whom the greater part of this work has been carried out, has published recently a report of the findings of this investigation, which report shows diethyl sulfate to be a most satisfactory general reagent for introducing ethyl groups into organic compounds.

Mellon Institute will be pleased to furnish samples of this material to those interested, and Mr. Cade will correspond gladly with any one who desires further information upon this subject. Reprints of the article referred to may be obtained by writing to Mr. Cade at the institute.

U. S. Patent 1,355,103 (October 5, 1920).

The Surface Tension Balance[1]

Apparatus for the Rapid Measurement of Surface Tension

By **Robert Gladding Green**

University of Minnesota, Minneapolis, Minn.

A new type of surface tension balance is described, an apparatus utilizing the drop weight method of measuring surface tension of liquids. Less than five drops of liquid are necessary for measurement. No calculations are used and the drop weights are not actually determined. The surface tension is indicated upon the scale directly in dynes per centimeter.

WITH the increasing application of physical and colloidal chemistry to biological science and the industries, surface phenomena are being recognized as of great importance and the measurement of surface tension is accordingly becoming a very common procedure. Experimental work involving large numbers of surface tension determinations has been carried on in these laboratories for a number of years, and a special study has been made to develop apparatus and methods suitable for biochemical investigation. While rapidity of measurement has been considered of prime importance, it has been required that the procedures give standard values of reasonable accuracy. For results of different investigations and of various investigators to be comparative, it is essential that data be reported in true standard units. All methods of surface tension measurement require correction to give standard values, but as the correction in case of the drop weight method can be made so small as to be negligible, this method has been adopted for general use. For use with the drop weight method two types of torsion wire balances have been developed. Such an apparatus has been termed a surface tension balance.

A torsion wire balance was used by Searle[2] for the measurement of surface tension, the degree of torsion being determined by the use of weights. DuNuoy[3] introduced the production of torsion in one end of the torsion wire, and also its indication by means of a scale divided into degrees. In a preliminary description of this apparatus[4] an adjustable scale has been introduced, which has made it possible to express the torsion of the wire in standard units of surface tension so that readings are made directly in dynes per centimeter.

Description

The two types of our surface tension balance are designated as Type A and Type B. The apparatus built as used in these laboratories is easily convertible from one type to the other. In general, the apparatus consists of three mechanical parts, a dropping pipet, a balance beam mounted upon a torsion wire, and an adjustable scale. The dropping pipet is similar to those used for actual drop weights. The balance beam (*CB*, Fig. 2) supported by the torsion wire *D* carries at one end a silver cup, *C*, pivoted upon watch jewels. The adjustable scale consists of a series of arcs of the same radius, but the segments are of different lengths and each segment is divided into the same number of units by lines normal to the arcs. This division into units is different in Type A and Type B. The scale face is movable horizontally so that any one of the series of arcs can be moved under the end of the pointer. The scale is so constructed in relation to the size of the torsion wire that the units represent surface tension in dynes per centimeter.

Type A balance is similar in design to the apparatus described in the preliminary paper.[4] Here the balance beam swings to an angular position when a drop of the liquid to be measured is dropped into the cup. The adjustable scale is so placed that the end of the beam opposite the cup acts as a pointer and swings over the scale face indicating the surface tension in dynes per centimeter. At the angular position of equilibrium the force acting upon the balance beam may be expressed by the equation $\Theta c = w\gamma \cos\Theta$, where Θ = angle of torsion of the wire, c = torsion constant of the wire, w = weight of liquid drop used, and r = length of balance beam from torsion wire to cup. This may be written $w = k\frac{\Theta}{\cos\Theta}$, as c and r are constants. We also have Tate's law, $\gamma = kw$, where γ = surface tension and k = constant. Combining the two equations, we have $\gamma = k\frac{\Theta}{\cos\Theta}$.

This relation indicates that a scale reading surface tension directly in dynes per centimeter when used on this type of balance must be so constructed that the size of the units will decrease as the angle of torsion increases. As the relation between Θ and $\cos\Theta$ is purely geometrical, such a scale can be accurately constructed, and is pictured in Fig. 1.

Type A surface tension balance is the simplest and most rapid to operate. It has a limitation of accuracy as the function $\Theta/\cos\Theta$ decreases rapidly with large values of Θ.

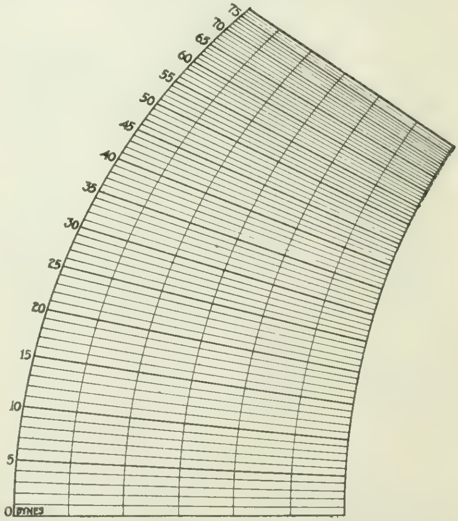


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Fig. 1 Scale on Type A Balance

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[1] Received April 28, 1923.

[2] *Proc. Cambridge Phil. Soc.*, **17**, 285 (1914).

[3] *J. Gen. Physiol.*, **1**, 521 (1919).

[4] *J. Bact.*, **7**, 367 (1922).

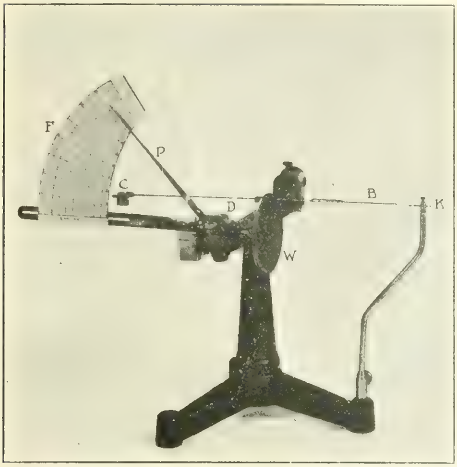

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FIG. 2—TYPE B SURFACE TENSION BLOWER

This type of apparatus is calibrated by the use of a standard solution, preferably with a low surface tension, as benzene, and finds its application where rapidity and ease of manipulation is desired.

Type B apparatus is pictured in Fig. 2. In this type the balance beam at equilibrium is in the horizontal position, the zero point being determined by the indicator *K*. Angular displacement of the balance beam due to the weight of the liquid dropped into the cup is counterbalanced with torsion produced by rotation of one end of the wire. As torsion is produced in the wire by means of the wheel *W*, the pointer *P* moves over the scale face and indicates the surface tension of the liquid in dynes per centimeter when the balance beam is again in the horizontal position. At equilibrium the balanced forces are expressible in the notation used above as $\Theta c = wr$, and combining this with the law of Tate, $\gamma = k\Theta$, indicating that in this type of apparatus the units representing surface tension are proportional to the angles of torsion. Such a scale is shown constructed in Fig. 3.

CALIBRATION

The pointer is set at zero dynes and the balance beam brought opposite the horizontal indicator. Two or three drops of pure water (or other standard liquid of known surface tension) are dropped from the dropping pipet into the cup. The beam is balanced in the horizontal position by torsion in the end of the wire, the pointer moving to some angular position upon the scale face. In the case of water at 25° C., this angular displacement represents 72.8 dynes. On the scale face among the series of arcs there will be found one which will correspond to this angular displacement and will be divided into 72.8 units. The scale face is moved laterally until the reading off the end of the pointer is 72.8 and the apparatus is calibrated. This process is carried out quickly and conveniently each time the balance is used or the pipet cleaned, and it is also desirable to check the calibration after running a series of measurements. The pipet is the only part of the apparatus to be cleaned, as the cup need only be dried and the balance beam checked for zero reading. With pure water and careful manipulation repeated calibrations of the instrument will check within one or two tenths of a dyne.

The number of drops used depends upon the size of the torsion wire; two or three drops have been found very convenient. The adjustability of the scale allows for a variation of 30-degree angular displacement of the pointer, and this coupled with the choice of size of torsion wire used and the number of drops employed gives the apparatus great flexibility.

Evaporation and temperature are the gross sources of error. With water and watery solutions the evaporation error is minimized in that calibration and measurements are made under similar conditions of evaporation. The temperature error may be made small by control of room temperature or by frequent calibration.

It is essential that the water used in calibration of the apparatus be very pure, as minute traces of some substance markedly reduce surface tension. It has been practice to use freshly redistilled water for calibration of this instrument, accepting the surface tension of this liquid as 72.8 dynes at 20° C.

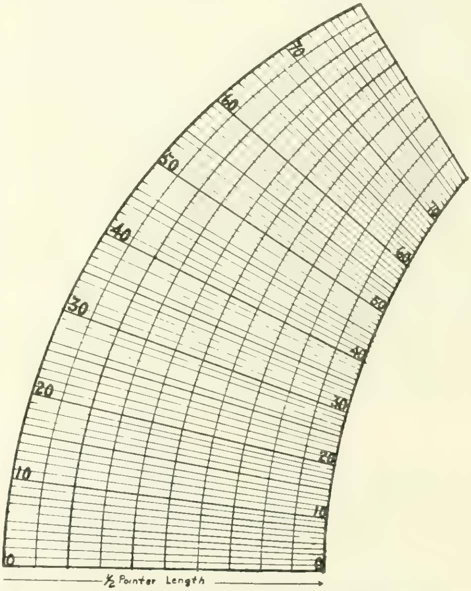

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FIG. 3—SCALE ON TYPE B BALANCE

ACKNOWLEDGMENT

The writer is indebted to Professor MacDougall, of the Department of Chemistry of the University of Minnesota, for many helpful and valuable suggestions.

New Uses for Wood

Chemical research is revealing new uses for wood that were not dreamed of a few years ago, declares the Forest Service, Department of Agriculture. One example is that of the extended use of pulpwood, not only for paper products, but also for fiber containers, wall board, and similar forms of material. Wood is already in use for the making of artificial silk, rope, carpets, and other fabrics.

The Viscosity of Coke-Oven Tars and Soft Pitches[1]

By Wilbert J. Huff

The Koppers Company, Pittsburgh, Pa.

In the utilization of tar and soft pitches as liquid fuel, probably no property influences the design of pumps, piping, and burners more than the change of viscosity with temperature; yet, to the chemist and engineer seeking information on this property very little is available in the literature.

This paper gives the results of a brief study of this property using a number of typical coke-oven tars and their very soft pitches. The results are expressed in such units that they may be applied directly to the calculation of the pressure drop in pipe lines. Directions and formulas covering such calculations are also appended.

The viscosity data should also prove useful for still and condenser design in connection with the carbonizing or tar-distilling plant.

The general shape of the viscosity-temperature curves for the tars and pitches when plotted on ordinary coördinates is illustrated by Fig. 1. The sharp bend is characteristic. The smooth yet rapid transition of the coal-tar pitch aggregate from a liquid so viscous that it is brittle to a mobile fluid resembles in general the corresponding change in typical emulsoid colloids, and there is at present little reason to doubt that high-temperature coal tar and its pitches are colloidal systems. Considering the wide industrial applications of these materials and the importance of physical properties in determining such applications, it is surprising that the theoretical development of these has received so little attention.

Today the industry is controlled by a series of empirical tests, such as float tests, penetration tests, so-called "melting point tests," slide tests, and "free carbon" tests, whose correlation is very imperfectly understood. This leads to considerable confusion in the compilation of specifications, and throws upon the industry a diversification of demands which entails heavy expense. Such empirical tests either deal largely and more or less directly with the change in viscosity with temperature, or, as in the case of "free carbon," deal with constitutive properties which affect the change of viscosity with temperature. The shape of the curve would, therefore, appear to be of interest to the manufacturer and purchaser of coal-tar aggregates.

Determination of Viscosity

Following German practice, coal-tar laboratories in this country have, in general, adopted the Engler viscometer. Recently the Saybolt Universal viscometer has met with favor. These instruments are, however, rather unsuited for the technical determination of the higher viscosities displayed by many tars at or near room temperature, or by pitches at temperatures often much higher than room temperature. To meet this need, such laboratories have generally employed the Stormer viscometer, and the data here presented were obtained by this instrument.

This is essentially a rotating cylinder driven by a known weight. It was described by Stormer[2] and by Rogers and Sabin[3] for the examination of paint. Its limitations have been discussed by Riggs and Carpenter.[4] Recently it has been used by Higgins and Pitman[5] for the determination of the absolute viscosities of pyroxylin plastics. The last-named writers found that the determinations, properly corrected, gave very satisfactory values provided the viscosities were greater than 15 centipoises.

The chief objection to the Stormer viscometer lies in the friction factor. With no liquid in the instrument, the spinning of the cylinder for 100 revolutions requires some time. Fig. 2 gives the time required for 100 revolutions with different driving weights with no liquid present. It shows, as expected, that with increasing driving weight the curve approached parallelism with the x-axis asymptotically, while with increasing times it approached parallelism with the y-axis asymptotically, and suggests a hyperbola. Determinations of points on the curve with driving weights less than 10 grams proved difficult, because slight variations in the character of the initial impulse seriously affect the time required for 100 revolutions.

Since the curve approaches parallelism with the respective axes with high driving weights and high times, the instrument appears capable of giving comparative viscosities under these conditions, especially when the driving weight remains constant throughout, a precaution observed in the experiments reported herewith.

Thus, Higgins and Pitman found that sufficiently high viscosities with high driving weights gave values which could be expressed by the straight-line equation $V = At - B$, where B is the correction factor.

An attempt to determine, for the instrument employed, the constants of the Higgins and Pitman equation, using as calibrating liquids two glycerol solutions having densities lying in the region from 1.20 to 1.23, however, gave a slight positive value for B. This may have been due to some unknown experimental error, or to the doubt which lies upon the true viscosities for solutions of glycerol in this region.[6]

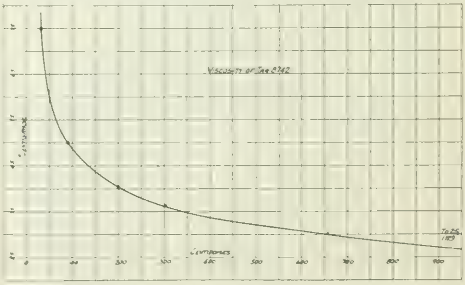

Fig. 1

The readings were, therefore, converted to absolute viscosities as follows:

> The time for a carefully calibrated petroleum oil having a viscosity of 29.9 centipoises was found to be 13.5 seconds with a driving weight of 126.9 grams. The weight necessary to over-

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[1] Presented before the Section of Gas and Fuel Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Oil, Paint Drug Rep.*, **27** (1911), through *Petroleum* **6**, 2184 (1920).

[3] This Journal, **3**, 737 (1911).

[4] *Ibid.*, **4**, 901 (1912).

[5] *Ibid.*, **12**, 587 (1920).

[6] Herschel, *Bur. Standards, Tech. Paper* **112**, 23.

come the friction of the empty viscometer at a time of 13.5 seconds was determined from Fig. 2 and subtracted from the driving weight. For each observation a similar correction was made. When the time was greater than 25 seconds a constant value was subtracted. The absolute viscosity was then calculated as follows:

$$29.9 \times \frac{\text{Observed time for tar or pitch}}{\text{Observed time for petroleum oil}} \times \frac{\text{Corrected weight for tar}}{\text{Corrected weight for petroleum oil}}$$

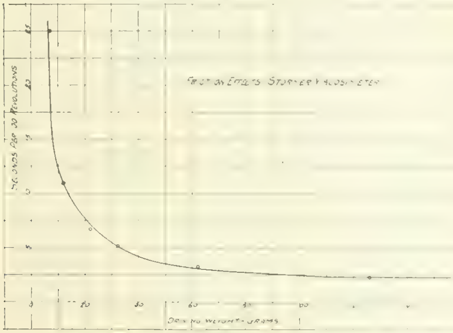

Fig. 2

This procedure is not entirely satisfactory and involves certain assumptions not strictly true. It does, however, give absolute viscosities sufficiently accurate for engineering purposes. Moreover, most of the viscosities of the tars and pitches measured are so high that they are undoubtedly comparative *inter se*. The general form of the interpolation equation to be discussed later is, therefore, not seriously affected by the friction correction.

Much of the criticism of Riggs and Carpenter against the Stormer viscometer may be dismissed, because it was based upon determinations made in the region where the friction correction curve undergoes a sharp bend. The instrument does, however, possess a number of faulty features. Thus, the bath is too small, making the maintenance of constant temperature difficult, and the mechanical suspensions faulty, so that it is necessary for the operator to be constantly on guard against improper alignments.

There is a great need for a satisfactory viscometer of this type. The absence of easily procured calibrating liquids of high viscosity has hitherto hindered the introduction of the McMichael viscometer.

Scope of the Data

A survey of present practice at a number of plants using tar as a fuel showed that these installations in general had little or no difficulty in handling this material when its viscosity was less than approximately 100 centipoises, but that pumping troubles were generally encountered when the viscosity rose above this figure. This study was, therefore, directed towards the shape of the viscosity–temperature curve in this region.

The pitches examined were representative distillation residues whose viscosity in general could be reduced to approximately 100 centipoises or less within the range of steam heating.

Viscosity–Temperature Curve

Figs. 3 and 4 illustrate typical data so obtained. The viscosity–temperature relationships can best be shown graphically on log-log coördinates in which the temperature in degrees centigrade is plotted against the viscosity in centipoises, since the resulting graph is a flat curve which for all practical purposes may be regarded as a straight line. Thus, for interpolation purposes, the viscosity–temperature equation may be expressed as

$$\log z = \log K - n \log T_c \text{ or } z = \frac{K}{T_c^n}$$

where z is the viscosity, K is a constant, n is a constant, and T_c is the temperature in degrees centigrade.

A similar equation is given by Bateman[7] for the change in the viscosity of high-boiling creosote and carbolineum oils with change in temperature. It is perhaps of interest to point out that these interpolation equations form only a special case of the rather general empirical equation employed by Thorpe and Rodgers in their classical work on viscosity—viz.,

$$z = \frac{a}{(b + T_c)^n}$$

This was first proposed by Slotte.[8, 9]

In order to indicate possible variations in the character of the viscosity–temperature curves for a number of different tars and their soft pitches, the writer has plotted such data. In every case the points on log-log coördinates obeyed approximately the straight-line relationship shown on Figs. 3 and 4.

From the slopes and intercepts of the various straight lines the following approximate values for K and n were deduced:

Condition	Logarithm of K[a]	Logarithm of n
	Tar 8742	
Raw tar	8.23	3.66
20.2% oil off	16.10	7.03
22.7% oil off	16.25	7.00
26.2% oil off	16.90	7.22
	Tar 9522	
Raw tar	8.04	3.56
15% oil off	13.52	5.80
18% oil off	13.82	5.85
20% oil off	14.90	6.30
	Tar 9523	
Raw tar	8.05	3.52
19% oil off	14.50	6.20
22.3% oil off	16.00	6.85
26.2% oil off	18.30	7.25
	Tar 9524	
Raw tar	6.10	2.58
21.2% oil off	12.90	5.65
22.6% oil off	13.15	5.65
27% oil off	14.40	6.20
	Tar 9525	
Raw tar	10.52	4.44
7.2% oil off	15.50	6.59
14.2% oil off	17.20	7.06
	Tar 10859	
Raw tar	6.98	3.13
22.6% oil off	12.30	5.26

[a] All logarithms given have 10 as the base.

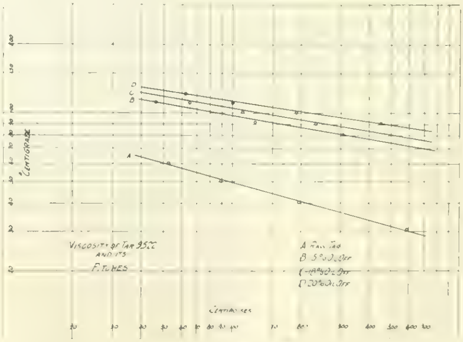

Fig 3

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[7] *U. S. Dept. Agr., Bull.* **1036**, 54.

[8] Bingham, "Fluidity and Plasticity," **1922**, p. 130. McGraw-Hill Book Company, New York City.

[9] A more exact approximation curve would probably be obtained if this general equation were used. It is, however, cumbersome.

It should of course be remembered that these constants apply only to temperature and viscosity conditions within or near the limits adopted for this study.

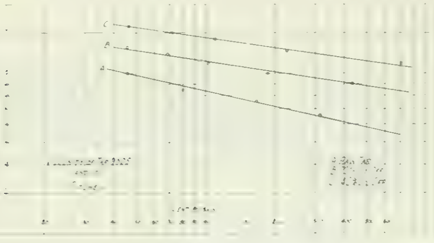

Fig. 4

Viscosity of Tar and Other Properties

The variation in viscosity from tar to tar suggests the interesting possibility of some correlation between this property and other properties. Unfortunately, data upon these tars were accumulated to meet certain technical exigencies, and, at the time, the compilation into a viscosity-temperature study was not contemplated, so certain relationships which might be of interest could not be developed. Following is some of the information available:

Tar No.	Specific Gravity at 15.5°/4° C.	Water %	Free Carbon %	Crude Tar Acids %	Naphthalene Cake %	Anthracene Cake %
8742	1.183	1.5	4.86	2.6	3.2	1.6
9522	1.149	2.3	(a)	1.5	2.5	1.5
9523	1.165	1.5	7.07	1.7	4.3	...
9524	1.163	1.0	6.35	0.3	10.5	
9525	1.237	3.0	(b)	0.7	3.5	1.2
10859	1.166	2.0	....	1.4	5.8	1.9

a Another sample gave 4.28 per cent free carbon.
b Another sample gave 11 per cent free carbon.

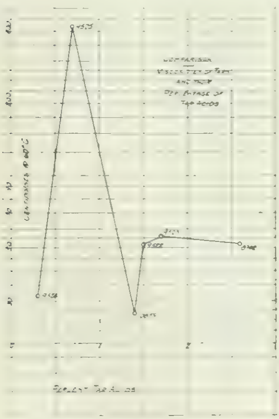

Fig. 5

The relative oil-pitch yields may be judged by reference to the table of constants just preceding.

The percentages of tar acids given are the percentages of crude acid actually recovered from the 170° to 235° C. fraction, while the percentages of naphthalene represent the weights of dry naphthalene cake actually recovered from the 170° to 270° C. fractions. The distillations were made in a 5 × 7.5 inch, Jayne type, tar still, using a 400° C. thermometer, meeting the thermometer specifications of A. S. T. M. D-20-18. All data were calculated upon the raw tars, save the free-carbon values. These were calculated upon the dehydrated tars, as is customary in free-carbon tests.

It is generally held that the viscosity of a coal tar is related to its specific gravity and its free-carbon content. Unfortunately, data upon the free-carbon content of these tars were not complete. For another series of tars, however, viscosity,[10] specific gravity, and free-carbon data were available and these are shown graphically in Figs. 7 and 8. A graphic comparison between the viscosities of the tars listed above and their percentages of crude tar acids and crude naphthalene cake is shown in Figs. 5 and 6.

The data are insufficient to formulate a complete explanation of the viscosity of coke-oven tars and their pitches and the change of viscosity with temperature. If speculation is in order, it is interesting to suppose that the pyrogenetic polymerization of the oils and simple chemical compounds to the pitch bitumens, with the attendant formation of free carbon and increase in density, brings an increase in the average size of the constituent particle, with an increase in viscosity. The decrease in viscosity with rising temperature may be due largely to a degeneration of the loosely bound bituminous aggregates.

Whether such speculation may in the future be shown to have a firm foundation in fact or not, the data just presented indicate that an association does exist between the viscosity, free-carbon content, and specific gravity, but that such an association is by no means exact. The quantity of any simple chemical individual, such as naphthalene or phenol, is apparently not indicative of the viscosity.

The exceptionally viscous tar listed above (9525) is high in free-carbon content, water content, specific gravity, pitch yield, low in oil yield, and rather low in naphthalene and tar acids.

Change of Viscosity of Tars and Pitches with Changing Oil Content

The experimental values detailed here do not show accurate correlation between the volume of the oil distilled from the tar and its increase in viscosity with such distillation. This is no doubt partly due to the fact that distillation losses of varying magnitudes occurred in the preparation of the pitches, but many other factors enter. Thus, it is well known that the oils themselves undergo an increase in viscosity with continued heating, ultimately giving the pitch resins or the free carbon, and that this increase depends upon thermal conditions and other variables. The character of the pitch obtained at a given oil yield may therefore vary with distillation conditions. A minor error is the partial crystallization of the distillates.[11] Our present information is too limited to permit a correlation to be calculated from any theoretical considerations.

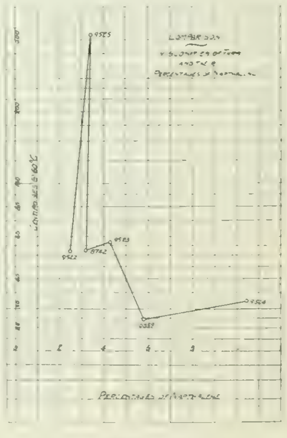

Fig. 6

The tar distiller and the project engineer, however, will find it necessary to estimate this change in some manner. Given the viscosities of the tar and one pitch, a simple method of approximating the viscosity of a pitch not greatly different is to assume that the change in temperature for viscosities of approximately 100 centipoises is linear with the amount of oil distilled from the tar. The new curve is then drawn on log-log coördinates parallel to the pitch curve already known.

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[10] The viscosities shown in Figs. 7 and 8 were determined by means of the Saybolt Universal viscometer.

[11] Huff, This Journal, 10, 1017 (1918).

In cut-back operations, where the oil is added to the pitch and the viscosity of each is known, the viscosity of the mixture may be calculated from an equation given by Bateman[12]—viz., $V_m = (V_t^p)(V_c^{1-p})$ where V_m is the viscosity of the solution, V_t the viscosity of the tar, and V_c the viscosity of the oil, and p is the percentage of tar used expressed as a decimal.

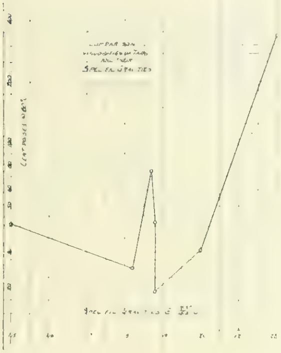

Fig. 7

Application of the Viscosity-Temperature Data in Design

The application of viscosity temperature data to engineering problems in the design of piping is so important and so often misunderstood that a brief abstract of a satisfactory procedure appears to be justified.

The movement of liquids in tubes may occur in either of two conditions, viscous (straight line flow) or turbulent flow. The first is expressed by the law of Poiseuille:

$$P = \frac{0.000668\, zlv}{D^2}$$

and the second by the modified Fanning equation:

$$P = \frac{0.323\, flsv^2}{D}$$

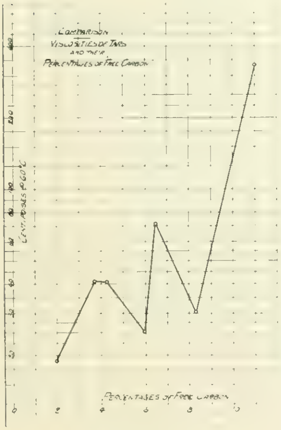

Fig. 8

where P = pressure drop (pounds per square inch)
z = viscosity of the liquid (in centipoises)
s = specific gravity of the liquid (referred to water at 4° C.)
l = length of pipe (feet)
D = inside diameter of the pipe (inches)
v = average linear velocity in pipe line (feet per second)
f = Fanning friction factor

Between these two conditions there exists a critical region which for commercial pipe lines is fixed by the relationship $\frac{Dvs}{z}$ = approximately 0.12. In this region the flow is irregular and may take on the characteristics of either region. Blausius has pointed out that the equations take the same form if $f = 0.00207\, \frac{z}{Dvs}$. This applies to viscous flow. A number of experimenters have developed relations between $\frac{Dvs}{z}$ and turbulent flow effects. At the suggestion of W. K. Lewis, this correlation has recently been investigated in detail and applied to commercial installations by a group of workers at the Massachusetts Institute of Technology. The results of this work were published by Wilson, McAdams, and Seltzer.[13] These show that the turbulent flow curve for commercial pipe lines may be approximated by the equation:

$$f = 0.01\left(\frac{z}{Dvs}\right)^{0.2}$$

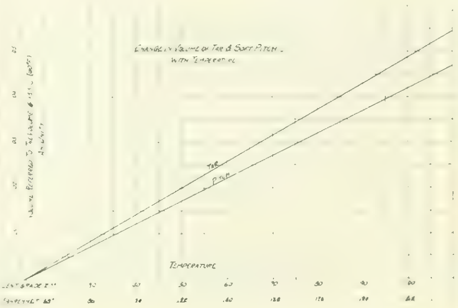

Fig. 9

or more exactly by the equation

$$f = 0.0035 + 0.00594\left(\frac{z}{Dvs}\right)^{0.424}$$ [14]

A graph for this equation is given in the paper cited.

With this information it is possible to calculate readily the pressure drop in pipe lines conveying tars or pitches in either viscous or turbulent flow.[15]

The first step involves the calculation of $\frac{Dvs}{z}$. If this is less than 0.12, showing viscous flow, the Fanning friction coefficient is calculated by the equation of Blausius given above—namely, $f = 0.00207\, \frac{z}{Dvs}$. If it is greater than 0.12, the value of f for turbulent flow is calculated according to the appropriate equation of Wilson, McAdams, and Seltzer.

If the pipe line contains 90-degree elbows and the flow is turbulent, a correction equal to 30 diameters for each elbow is added to the length of straight pipe. If, however, the flow is viscous, data given by the last-named authors show that this correction factor drops off to a value of approximately 2.5 diameters where $\frac{Dvs}{z}$ is 0.003 or less. Between the coordinates diameter 30, $\frac{Dvs}{z} = 0.12$; and diameter 2.5, $\frac{Dvs}{z} = 0.003$; on log-log paper, this correction curve approximates a straight line. For values of $\frac{Dvs}{z}$ below 0.003, 2.5 D may be taken as the correction.[16]

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[12] *U. S. Dept. Agr., Bull.* **1036**, 83.

[13] This Journal, **14**, 105 (1922). The writer is indebted to this article for the information contained in this section.

[14] A very similar equation had previously been proposed by Lees for turbulent flow in smooth pipes.

[15] At the higher viscosities, tar and pitch may take on the properties of a plastic solid. It therefore appears advisable to so design the piping equipment that viscosities of 100 centipoises or less may be always secured Cf. A. Pochettino, *Nuovo cimento*, **8**, 77 (1914), from *C. A.*, **11**, 2980 (1917).

Knowing f and the corrected value for l, it is then only necessary to substitute these values in the Fanning equation:

$$P = \frac{0.323\, flsv^2}{D}$$

This is done irrespective of whether the flow is viscous or turbulent.

Coal tar and its pitches show a tendency to deposit solid matter on horizontal surfaces, thus restricting the effective diameter. Accordingly, a large factor of safety should be allowed in the application of these calculations.

SPECIFIC GRAVITIES OF TARS AND PITCHES

To apply this procedure it is necessary to have some information on the specific gravities of the tars and pitches and the change of specific gravity with temperature. Above are given some typical specific gravities for raw coke-oven tars at 15.5° C. The change in specific gravities with temperature can be calculated by reference to Fig. 9, which shows approximately the change in volume of an average coke-oven tar and of an average soft pitch with change in temperature. Values so represented are only approximate, because the coefficient of expansion varies with the tar and pitch and also with the temperature, but present information does not justify refinements beyond simple linear relations as shown, and these are probably sufficiently accurate for all ordinary engineering data.

The specific gravity of the pitch residue at 15.5° C. rises rapidly at first as the water and lighter oils are distilled from the tar; after that it changes rather slowly as the specific gravity of the distillate approaches the specific gravity of the residue. The change in specific gravity, like the change in viscosity, is probably influenced by the polymerization of the oils during distillation.

Following are some typical specific gravities:

Tar 9522		Tar 9524	
Condition	Specific Gravity at 15.5°/4° C.	Condition	Specific Gravity at 15.5°/4° C.
Raw tar	1.149	Raw tar	1.16
15% oil off	1.214	21.2% oil off	1.233
18% oil off	1.215	22.6% oil off	1.243
20% oil off	1.222	27% oil off	1.246

ACKNOWLEDGMENT

The writer wishes to express his thanks to G. G. Désy, who distilled some of the tars and made some of the determinations included here.

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[16] If l is less than 300 diameters, further corrections must be applied. See Herschel, *Proc. Am. Soc. Civil. Eng.*, **84**, 527 (1921), from Wilson, McAdams and Seltzer, *Ibid.*, **84**, 118 (1921).

Higher Alcohols from Petroleum Olefins[1]

By W. W. Clough and Carl O. Johns

STANDARD OIL COMPANY OF NEW JERSEY, ELIZABETH, N. J.

This paper presents the chemical properties and physical constants of some secondary higher alcohols manufactured from the olefins formed in the commercial cracking of petroleum oils. New azeotropic mixtures of some of these alcohols with water and with the alcohols and their acetates are described. The alcohols obtained by this process thus far have all been normal secondary alcohols. The availability of this series of alcohols, all of which have hitherto been very rare, should furnish the organic chemist with raw materials for the synthesis of a wide range of organic compounds. A few derivatives of the alcohols are described and some of these will add to our list of organic solvents. This process constitutes one of the few cases in which the by-products of the petroleum refinery have been employed on a commercial scale for the synthesis of organic compounds.

CRUDE petroleum is practically devoid of olefins, but these compounds are formed in large quantities in the pyrolytic decomposition of mineral oils at elevated temperatures. Since pyrolysis is carried out on an extensive scale in the cracking of the heavier oils to produce gasoline, a very large supply of olefins is available from this source.

The chemistry of cracking of oils is not fully known, since the decomposition may proceed in various ways according to the conditions employed and the chemical constitution of the molecules which are cracked. There is evidence, however, that in its simplest form cracking consists in the splitting of the large molecules into saturated and unsaturated hydrocarbons. Thus, decane might decompose into pentane and amylene as follows:

$$\underset{\text{Decane}}{CH_3.(CH_2)_8.CH_3} = \underset{\text{Pentane}}{CH_3.(CH_2)_3.CH_3} + \underset{\text{Amylene}}{CH_3.(CH_2)_2.CH = CH_2}$$

Olefins combine with sulfuric acid to form alkyl acid esters and when such acid esters are hydrolyzed they produce alcohols and sulfuric acid. These reactions may be shown as follows:

$$\underset{\text{Propylene}}{CH_3.CH = CH_2} + H_2SO_4 = \underset{\text{Secondary propyl sulfuric acid}}{CH_3.CH(HSO_4).CH_3}$$

$$CH_3.CH(HSO_4).CH_3 + H_2O = \underset{\text{Isopropyl alcohol}}{CH_3.CHOH.CH_3} + H_2SO_4$$

The discovery by Mann and Williams,[2] that a mixture of a mineral oil and sulfuric acid promotes the formation of esters, is an important step in the development of a practical process of manufacturing alcohols from refinery gases. Working under assigned patents, the Standard Oil Company of New Jersey has developed and is operating a commercial process for the manufacture of higher alcohols from the olefins in pressure still gases. Many difficulties had to be overcome in transferring the process from a laboratory to a commercial scale. The success which has been attained is chiefly due to the persistent efforts of M. D. Mann, Jr., who designed the alcohol plant and has charge of it.

The gases which are used for the manufacture of the alcohols contain a mixture of olefins from which isopropyl and secondary butyl, amyl, hexyl, heptyl, and octyl alcohols are obtained. These are produced in decreasing proportions in the order just stated. All of these alcohols made thus far in a pure state have been normal secondary alcohols—that is, alcohols containing the hydroxy group on the second carbon atom of a straight-chain hydrocarbon. Although ethylene is present in the gases, there is no evidence of the formation of ethyl alcohol as the process is now operated.

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[1] Presented before the Division of Petroleum Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] U. S. Patent 1,365,043 (1921).

ISOPROPYL ALCOHOL, 2-PROPANOL

The rectified alcohol[3] is obtained as a constant boiling mixture containing 91 per cent of alcohol and 9 per cent of water by volume. This mixture boils at 80.4° C. and has a specific gravity of 0.816 at 20°/4° C. It is easier to dehydrate than is ethyl alcohol and a short digestion with excess of caustic soda and subsequent distillation gives a practically anhydrous alcohol which boils at 82.4° C., with a specific gravity of 0.785 at 20°/4° C. Isopropyl alcohol is miscible in all proportions with water, but may be salted out by saturating the solution with sodium chloride or other salts or with sodium hydroxide. The isopropyl alcohol now marketed is a colorless liquid having a somewhat bitter taste and a characteristic alcoholic odor different from that of ethyl alcohol but pleasant and free from the odors of the crude product.

AZEOTROPIC MIXTURE OF ISOPROPYL ALCOHOL AND ISOPROPYL ACETATE—This constant boiling mixture has not hitherto been described. It boils at 80.1° C. and 760 mm., and consists of 52.3 per cent of isopropyl alcohol and 47.7 per cent of isopropyl acetate by weight. It has a specific gravity of 0.8191 at 20°/4° C. It has a pleasant odor and is an excellent solvent for many organic compounds.

ISOPROPYL CHLORIDE[4]—This compound is easily made by slowly distilling a mixture of isopropyl alcohol and concentrated aqueous hydrochloric acid. To insure the best results it is necessary to employ a column of sufficient fractionating capacity to permit the chloride to distil over with as little alcohol as possible. This is relatively easy since the chloride boils at 36.5° C. and the alcohol at 80.4° C. Isopropyl chloride is an excellent solvent for fats, and while it may be ignited it burns slowly and the flame is easily extinguished.

SECONDARY BUTYL ALCOHOL, 2-BUTANOL

This alcohol, which has been known hitherto only as a rare laboratory chemical, is now available in commercial quantities at a low price. Former investigators usually prepared it for experimental purposes by reducing methylethyl ketone with sodium. This method was used by Norris and Green,[5] who have published an extensive investigation on this alcohol and its derivatives. In a recent very excellent paper, Brunel, Crenshaw, and Tobin[6] state that they prepared secondary butyl alcohol from the corresponding ketone by reduction with hydrogen under pressure, using nickel oxide as catalyst.

AZEOTROPIC MIXTURE OF SECONDARY BUTYL ALCOHOL AND WATER—When the aqueous solution containing the mixture of soluble alcohols resulting from the hydrolysis of the acid esters is rectified, the constant boiling mixture of isopropyl alcohol and water distils over at 80.4° C. From this residue, if sufficient water is present, the secondary butyl alcohol distils over as a constant boiling mixture with water at 87.5° C.

As far as the writers have been able to ascertain, this azeotropic mixture is not described in the literature. It was discovered by Mann and Lebo in the alcohol plant of this company while fractionating an aqueous solution which contained chiefly secondary butyl alcohol admixed with a small proportion of other alcohols. The initial fractionation was made on a charge of 1000 gallons with a 30-plate, 20-foot fractionating column. A portion of this distillate was later re-run in a glass laboratory still, which has also been used for the final fractionation of the other distillates described in this paper. This still was designed by Buc and consists of a glass column 2 meters high and of 5 cm. internal diameter. The column is filled with glass tubes with an internal diameter of about 5 mm. and 25 mm. long. These tubes are constricted somewhat at both ends and are placed in the column so that the liquid will readily drain out of them. This fractionating column can readily be adapted to stills of different sizes.

A portion of the secondary butyl alcohol which had previously been fractionated in the large still was re-run in the glass still and was found to boil at a constant temperature of 87.5° C. and 760 mm. It had a specific gravity of 0.8620 at 20°/4° C. and contained 72.7 per cent of alcohol by weight and 77.72 per cent by volume.

PURIFICATION AND DEHYDRATION OF SECONDARY BUTYL ALCOHOL—The first lot of pure anhydrous alcohol was prepared by drying over sodium hydroxide a mixture consisting of isopropyl, secondary butyl, and a small proportion of still higher alcohols. This did not remove all the water, but on distillation the isopropyl alcohol carried over some water and as the temperature rose the remainder was carried over with the first portion of the secondary butyl alcohol. It was very easy to obtain pure anhydrous secondary butyl alcohol in this manner by fractionating three or four times. A second lot of pure alcohol was prepared by dehydrating the azeotropic mixture of secondary butyl alcohol and water with sodium hydroxide and then distilling the alcohol over aluminium amalgam. This method gave pure anhydrous alcohol very readily.

DETERMINATION OF THE BOILING POINT OF THE ALCOHOL—Since ample quantities of secondary butyl alcohol which had been purified by the foregoing methods were available, the boiling point determinations were made by means of the glass still previously described, using two accurate Anschutz thermometers. The boiling point of both lots of purified alcohol was 99.40° C. at 760 mm. Brunel, Crenshaw, and Tobin obtained 99.53° C. at 760 mm. The value for $\frac{dT}{dp}$ in degrees per millimeter pressure was 0.036, or the same as that found by these authors.

DETERMINATION OF SPECIFIC GRAVITY—Determinations were made in a 50-cc., vacuum-jacketed specific gravity bottle. The following results were obtained:

D 15°/4° C.	*D* 20°/4° C.	*D* 25°/4° C.
0.8104	0.8063	0.8027

The density at 25° C. agrees with that obtained by Brunel, Crenshaw, and Tobin.

The following alcohol-water mixtures were made by weighing the alcohol and water in a glass-stoppered bottle, and the specific gravities were determined at 20°/4° C.:

Per cent Alcohol by Weight	*D* 20° 4° C.
100.00	0.8063
89.50	0.8281
79.60	0.8465
69.31	0.8682
64.17	0.8797
Immiscible	
17.85	0.9732
10.00	0.9842
0.00	0.9982

The results were plotted to a large scale on cross-section paper so that 0.01 per cent of the volume and 0.0002 of the specific gravity could be read. These points were connected by a smooth curve and from this the following table was constructed. The temperature correction table was constructed by taking the specific gravities of the alcohol-water mixtures at 15°/4°, 20°/4°, and 25°/4° C.

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[3] Grant and Johns, *Am. J. Pharm.*, **94**, 418 (1922), Lebo, *J. Am Chem. Soc.*, **43**, 1005 (1921); Curme, *Chem. Met. Eng.*, **25**, 1049 (1921).

[4] Linneman, *Ann.*, **136**, 41 (1865); Grant and Johns, *Am. J. Pharm.*, **94**, 424 (1922); U. S. Patent 1,436,377 (1922).

[5] *Am. Chem. J.*, **26**, 301 (1901).

[6] *J. Am. Chem. Soc.*, **43**, 561 (1921).

TABLE I—SPECIFIC GRAVITY OF SECONDARY BUTYL ALCOHOL-WATER MIXTURES AT 20°/4° C.

Per cent by Weight	Per cent by Volume	Specific Gravity
0	0	0.9982
1	1 24	0.9968
2	2.47	0.9954
3	3.70	0.9940
4	4.92	0.9926
5	6.14	0.9912
6	7.36	0 9898
7	8.58	0.9884
8	9.79	0.9870
9	11.00	0.9856
10	12.21	0.9842
11	13.41	0 9828
12	14.61	0.9814
13	15.80	0.9800
14	16.99	0.9786
15	18 18	0.9772
16	19.36	0.9758
17	20.54	0.9744
17.85	21.55	0.9732
	Immiscible	
64.17	69.97	0.8792
65	70.74	0.8775
66	71.67	0.8756
67	72.59	0.8737
68	73.51	0.8716
69	74.42	0.8696
70	75.32	0.8675
71	76.21	0.8655
72	77.10	0.8634
73	77.99	0.8614
74	78.87	0.8594
75	79.75	0.8574
76	80.63	0.8554
77	81.50	0.8534
78	82.36	0 8514
79	83.22	0.8493
80	84.07	0.8473
81	84.92	0.8453
82	85.76	0.8433
83	86.60	0.8413
84	87.44	0.8393
85	88.27	0.8373
86	89.09	0.8352
87	89.90	0.8332
88	90.71	0.8311
89	91.51	0.8291
90	92.31	0.8270
91	93.10	0.8249
92	93.89	0.8229
93	94.67	0.8208
94	95.45	0.8188
95	96.22	0.8167
96	96.99	0.8147
97	97.76	0.8127
98	98.52	0.8106
99	99.27	0.8085
100	100.00	0.8063

TABLE II—TEMPERATURE CORRECTION
(Change in specific gravity per degree centigrade)

Strength Alcohol Per cent	Correction
10	0.00035
16	0.00044
Immiscible	
65	0 00077
70	0.00077
80	0.00077
90	0 00077
100	0.00077

SECONDARY BUTYL ACETATE—This compound was made by refluxing 1 mol of secondary butyl alcohol with 1 mol of acetic anhydride until the reaction was complete. After washing with water, neutralizing with sodium carbonate, and drying over calcium chloride, the ester distilled at 112.2° C. and 760 mm. Norris and Green report a boiling point of this ester at 111.5° to 112° C. at 744 mm. The specific gravity of the ester obtained by the writers was 0.8701 at 20°/4° C.

AZEOTROPIC MIXTURE OF SECONDARY BUTYL ALCOHOL AND SECONDARY BUTYL ACETATE—The mixture boiled at 99.60° C. at 758 mm. and consisted of 86.3 per cent of secondary butyl alcohol and 13.7 per cent of the ester by weight. Its specific gravity at 20°/4° C. was 0.8137. It possessed a characteristic ester odor.

SECONDARY BUTYL CHLORIDE, 2-CHLORBUTANE—This compound was made in the same manner as isopropyl chloride and the reaction proceeded very easily. The boiling point of the chloride was 68° C.,[7] at 760 mm. It had a pleasant odor and was a good solvent for fats and waxes.

SECONDARY AMYL ALCOHOL, 2-PENTANOL

This was fractionated from a mixture containing the amyl alcohol together with some water and other alcohols. In this way a large fraction boiling between 118° and 120° C. was collected. This was refractionated until a constant boiling point of 119.2° C.[8] at 760 mm. was attained. This alcohol had a specific gravity of 0.8088 at 20°/4° C.

At 20° C., 100 grams of secondary amyl alcohol dissolved 11.2 grams of water and 100 grams of water dissolved 4.2 grams of the alcohol.

TABLE III—SPECIFIC GRAVITY OF SECONDARY AMYL ALCOHOL-WATER MIXTURES AT 20°/4° C.

Per cent by Weight	Per cent by Volume	Specific Gravity
89.8	91.67	0.8299
90	91.76	0.8295
91	92.59	0.8275
92	93.43	0.8255
93	94.26	0.8235
94	95.09	0.8214
95	95.92	0.8193
96	96.75	0.8172
97	97.57	0.8151
98	98.38	0.8130
99	99.19	0.8109
100	100.00	0.8088

SECONDARY AMYL CHLORIDE, 2-CHLORPENTANE—This compound was made in the same manner as isopropyl chloride and secondary butyl chloride. It boiled at 96° C.[9] at 760 mm. It also had a sweet odor and was a good solvent for fats and waxes.

SECONDARY HEXYL ALCOHOL, 2-HEXANOL

This alcohol was fractionated from a mixture of higher alcohols. A boiling point of 139.4° to 139.6° C.[10] was obtained. This is within 0.5 degree of the boiling points given in two of the three papers referred to. The alcohol had a specific gravity of 0.8159 at 20°/4° C.

ALCOHOLS HIGHER THAN HEXYL

After the removal of all the alcohols up to and including secondary hexyl from the mixture obtained in the alcohol process, there remains an oily liquid which contains alcohols still higher than those already described. From this residual liquid have been isolated two alcohols with the characteristics of secondary heptyl (2-heptanol), and secondary octyl alcohol (2-octanol). The properties of these two alcohols have not yet been definitely determined and further work is in progress.

HIGHER ALCOHOLS IN ORGANIC SYNTHESES

All the alcohols described here are now available in commercial quantities, with the exception of the hexyl, heptyl, and octyl. While they may be used as solvents, it is apparent to the organic chemist that the availability of these hitherto very rare alcohols opens up an extensive field for their use in organic syntheses. While only a few derivatives have been mentioned in this paper, several others have been prepared. It is probable that some of these alcohols or their derivatives may find use in cosmetics and pharmaceutical preparations.

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[7] Estreicher, *Ber.*, **33**, 438 (1901); Norris and Green, *Am. Chem. J.*, **26**, 307 (1901).

[8] Wagner and Saizew, *Ann.*, **179**, 319 (1875); Bieloboubek, *Ber.*, **9**, 925 (1876).

[9] Przewalski, *Chem. Zentr.*, **1909**, II, 793; Wagner and Saizew, *Ann.*, **179**, 321 (1875).

[10] Ponzio, *Gazz. chim. ital.*, **31**, I, 404 (1901); Sabatier and Senderens, *Compt. rend.*, **137**, 302 (1903); Zelinsky and Przewalski, *Chem. Zentr.*, **1908**, II, 1855.

Registration at Milwaukee

Arkansas	4	Massachusetts	34	Pennsylvania	45
Connecticut	8	Michigan	29	Rhode Island	5
California	5	Mississippi	1	South Dakota	1
Colorado	4	Missouri	17	Tennessee	4
Delaware	5	Montana	1	Texas	3
Georgia	3	Maine	1	Utah	1
Illinois	179	Nebraska	6	Virginia	3
Indiana	33	New Jersey	20	West Virginia	6
Iowa	27	Nevada	1	Washington	4
Kansas	3	New York	59	Wisconsin	192
Kentucky	2	New Hampshire	2	Washington, D. C.	32
Louisiana	6	North Dakota	2	Wyoming	1
Maryland	6	Oregon	3	New Mexico	1
Minnesota	32	Ohio	59	Canada	2

Guests	94
TOTAL REGISTRATION	946

Some Factors Which Affect the Plasticity of a Paint[1]

By Eugene C. Bingham and Alfred G. Jacques

Lafayette College, Easton, Pa.

It is practicable to express quantitatively the effects produced upon a paint by long continued grinding, by changing the concentration of pigment, by adding soaps, water, mineral oil, or deflocculating agents, etc. Since the yield value and mobility are independent properties, these factors affect now one of these properties, then the other, and sometimes both simultaneously. This independence and the occasionally prodigious magnitude of the effects enhance the importance of the plasticity method.

EARLIER work by Booge, Bingham, and Bruce[2] proved that when two paints are carefully prepared under supposedly identical conditions so as to be identical in other properties, the plasticities of the two paints may be considerably different. This work makes it highly desirable to conduct an intensive study of the factors which influence the plasticity.

CONDITIONS OF GRINDING

An Abbé ball mill revolving at 88.5 r. p. m. was used as in a previous investigation. The writers' effort has been confined to a study of the changes in plasticity with the time of grinding. Paint B was made to contain 65 per cent by weight of Gold Seal Bechton White Lithopone and 35 per cent of acid-refined linseed oil. The oil was first added, the pigment then stirred in, and finally the pebbles were added. The paint samples were removed periodically, evacuated, and measured with the Bingham and Green plastometer.

A second paint, C, was made with the same ingredients but with 60 per cent of lithopone and 40 per cent of oil. In this case only one-half of the pigment was added during the first half hour of grinding. The remainder was added in four portions with 3 minutes of grinding between each addition. The time of grinding was then reckoned from the time of the last addition.

TABLE I—CHANGE IN PLASTICITY OF A PAINT DURING GRINDING

Time of Grinding Hours	Mobility	Yield Value Dynes Sq. Cm.
Paint B, 65 per cent lithopone and 35 per cent acid-refined linseed oil Density = 1.885, temperature = 25° C., capillary No. 10[3]		
22.6	0.38	210
31	0.38	110
39	0.36	100
55	0.31	105
63	0.26	115
71	0.22	110
Paint C, 60 per cent lithopone and 40 per cent acid-refined linseed oil Density = 1.742, temperature = 25° C., capillary No. 13		
8	0.62	250
16	0.64	200
24	0.61	110
32	0.63	90
41	0.62	80
49	0.60	85
57	0.56	90

The method of adding the ingredients with Paint *C* is a decided improvement, for during the first part of the mixing the paint is stiff, with high yield value and low mobility, as will be seen later, and the ball mill may cease to function as a mixer. It is desirable, therefore, to have the concentration of pigment much lower at the start than later when the oil is thoroughly incorporated. It has been found experimentally that, even after several hours of attempted mixing, the paint may be so inhomogeneous that on subjecting it to shear in the plastometer the more mobile portions will flow out through the capillary, so that the paint remaining in the plastometer becomes continually stiffer. Needless to say, it is impossible to obtain consistent values during this stage in the mixing.

A summary of the data obtained from Paints B and C is given in Table I. The results prove that the yield value falls off rapidly as the grinding proceeds and reaches a constant value after a long time, much longer than was at first supposed, which under the conditions here employed is about 30 hours. The mobility increases at first slightly and then falls off. The maximum was reached in the writers' experiments in about 30 hours.

Bingham, Bruce, and Wolbach[4] ground a 65 per cent lithopone paint with acid-refined linseed oil for 16 hours, and obtained a yield value of 146 and a mobility of 0.36. They diluted this paint down to a composition of 60 per cent lithopone and 40 per cent oil, and obtained a yield value of 108 and a mobility of 0.62. The mobilities obtained by the writers agree fairly well with those of Bingham, Bruce, and Wolbach, but their yield values are considerably higher than the final yield value obtained by the writers, although not so high as the first values obtained. It is noted that the first yield value observed after many hours of grinding is more than 100 per cent higher than its final value.

TABLE II—CHANGE OF PLASTICITY WITH CONCENTRATION—25° C.

Weight Percentage of Lithopone	Mobility Observed	Mobility Calculated	Yield Value Observed	Yield Value Calculated
Paint F, Bechton White Gold Seal Lithopone of density 4.30, suspended in mineral oil containing 2 per cent of oleic acid, density 0.8751				
65.0	0.46	0.54	1010	980
62.5	0.53	0.60	810	840
60.0	0.64	0.66	720	710
55.0	0.78	0.78	430	440
50.0	0.96	0.90	280	170
45.0	1.03	1.02	230	0
35.0	1.30	1.27	115	..
25.0	1.63	1.51	95	..
15.0	1.78	1.75	40	..
0.0	2.11	2.11	0	.
Paint G, Bechton White Gold Seal Lithopone of density 4.30, suspended in a mixture of equal parts by weight of mineral oil and acid-refined linseed oil, density 0.9001				
65.0	0.43	0.49	970	970
62.5	0.54	0.57	820	810
60.0	0.63	0.64	650	650
55.0	0.75	0.79	315	320
50.0	0.93	0.93	270	0
45.0	1.09	1.08	120	..
35.0	1.42	1.37	40	..
25.0	1.67	1.66	20	..
15.0	1.96	1.95	0	
0.0	2.40	2.40	0	.

CONCENTRATION OF THE DISPERSE PHASE

Bingham, Bruce, and Wolbach[4] found simple relations when the yield values and mobilities of paints of different concentrations were measured. In their experiments only a single series of paints was obtained by dilution; hence, it was very desirable to confirm and extend their work and to determine whether similar results would have been obtained by direct grinding of samples instead of by dilution.

In order to use vehicles which are as widely different as possible, the writers have used a neutral mineral oil containing 2 per cent by weight of oleic acid for Paint F and a mixture of neutral mineral oil with an equal weight of acid-refined linseed oil for Paint G. Both paints were ground for 32 hours and other concentrations obtained by dilution. The results are summarized in Table II.

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[1] Presented before the Division of Physical and Inorganic Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Proc. Am. Soc. Testing Materials*, **22**, II, 420 (1922).

[3] *Ibid.*, **22**, 446 (1922).

[4] *J. Franklin Inst.*, **195**, 303 (1923).

These results are exactly similar to those of Bingham, Bruce, and Wolbach in the following respects:

1—The yield value-concentration curve is linear at the high concentrations, indicating that a zero yield value at a definite concentration of 48 per cent by weight in Paint F and 50 per cent by weight in Paint G might be expected as compared with a concentration of 43 per cent by weight obtained by Bingham, Bruce, and Wolbach.

2—The yield value-concentration curves invariably depart from linearity at low concentrations, so that every concentration of paint, no matter how small, shows a yield value. The pseudo-plastic condition[5] in paints therefore seems to be quite well established, even though it has not as yet been explained. It is not always easy to measure the efflux satisfactorily in the pseudo-plastic mixtures, but the values of the yield values seem to lie on a smooth curve.

3—The mobility-concentration curve is quite positively linear, pointing to a concentration of zero mobility of 81 per cent by weight for Paint F, 80.5 per cent for Paint G, as against 79.6 per cent by weight in the paint studied by Bingham, Bruce, and Wolbach.

This concentration of zero mobility would seem to be related to the volume of cubical close-packing,[6] which for equal spheres is 52.4 per cent by volume. It would appear that this concentration of zero mobility ought to be the same for any given disperse phase independent of the dispersion medium. In the three paints studied the volume concentration of zero mobility for lithopone turns out to be 46.4 per cent by volume for Paint F, 46.4 per cent by volume for Paint G, and 45.6 per cent by volume for paint studied by Bingham, Bruce, and Wolbach. This is very satisfactory agreement, the average value being close to 46.1 per cent by volume. That this value is so much less than the 52.4 per cent derived mathematically for equal spheres, may provisionally be attributed to the irregular shapes of the particles of the lithopone.

The mobilities of the three paints may be represented by the empirical formulas

Paint F, $\mu = \varphi (1 - 1.15\, n)$
Paint G, $\mu = \varphi (1 - 1.22\, n)$
Paint studied by Bingham, Bruce, and Wolbach, $\mu = \varphi (1 - 1.26\, n)$

where φ is the fluidity of the medium, and n is the fraction by weight of the disperse phase. It seems probable that the mobility of the suspension is determined by the fluidity of the medium, and one other factor which may be described as the free volume of the dispersion medium, in analogy with the free volume with which we have become familiar in pure liquids. The theory leads to a formula similar to that above except that the concentrations are by volume instead of by weight. This important peculiarity is as yet unexplained.

The mobilities as calculated by the foregoing formulas for Paints F and G are given in Table II, and the agreement between the observed and calculated values is very good.

The concentration of zero yield value as given above for Paints F and G is the same within the experimental error. This value is slightly higher than that obtained by Bingham, Bruce, and Wolbach. The concentration of zero yield value is affected by the size of particles of the disperse phase, but the yield value is very sensitive to the adhesion between the disperse phase and the dispersion medium, so that the approximate identity in these very diverse paints is remarkable. For example, if we compare these three paints at a 65 per cent concentration of pigment, we find that all of them have the same mobility—viz., 0.48—but the yield values are very different, 1010 for F, 970 for G, and 129 for the paint studied by Bingham, Bruce, and Wolbach. It therefore seems probable that the concentration of zero yield value is independent of the fluidity of the medium or of its adhesion to the pigment. It may therefore be solely dependent upon the individual particles.

It may be noted that the yield value-weight concentration curve departs from linearity at very different yield values in the different paints—viz., 400 dynes per sq. cm. for Paint F, 310 for Paint G, and 35 for the paint of Bingham, Bruce, and Wolbach. But the concentration in which this departure from linearity takes place is nearly the same, being 55 per cent for F, 55 for G, and 50 for the paint of Bingham, Bruce, and Wolbach.

The equations of the yield value-weight concentration curves are $f = 53.6\,n - 2510$ for Paint F, and $f = 66\,n - 3310$ for Paint G. The agreement between the observed and the calculated values is given in the last column of Table II.

PARTICLE SIZE

A few qualitative experiments seemed desirable to exhibit the effect of particle size on the yield value and mobility. For this purpose silica, normally used as a paint filler and known to have particles of large size as compared with the particles in lithopone, was ground in acid-refined linseed oil to contain 65 per cent by weight of silica and measured on the plastometer, at 25° C. The yield value was found to be 25 dynes per sq. cm., which is very much less than the yield value of 129 found by Bingham, Bruce, and Wolbach for the same concentration of lithopone. The mobility of the silica is 0.165, which is considerably less than the mobility of the same concentration of lithopone, 0.441. But the volume occupied by the two pigments is very different at the same weight concentration. We shall now therefore make the comparison at the same volume concentration. Assuming 2.30 as the density of the silica, the silica occupies 42.7 per cent by volume. This volume percentage of lithopone corresponds to a 75.7 per cent pigment by weight. This paint would have a mobility of 0.12 as calculated by formula and a yield value of 194. The mobilities are now nearly the same, and the yield value of the silica is 50 per cent higher than that of the lithopone. This small difference can be accounted for in a variety of ways, and is surprisingly small.

FLUIDITY OF MEDIUM

It has already been proved that temperature affects the mobility in the same ratio as it affects the fluidity of the medium, and that it does not affect the yield value. This conclusion is so important and so inherently improbable that it seemed desirable to suspend the same pigment in two oils of widely different fluidity, for which purpose blown linseed oil and lithopone have been used to compare with the lithopone paint in acid-refined linseed oil. A 35 per cent paint gave a mobility which remained constant after 7 hours of grinding, so that four successive samples gave the closely agreeing mobilities 0.0200, 0.0204, and 0.0198. The yield values read were also in good agreement, but the yield value is almost negligible, having an average value of 7 dynes per sq. cm. The 35 per cent of lithopone suspended in acid-refined linseed oil studied by Bingham, Bruce, and Wolbach had a yield value of 7.7 and a mobility of 1.40. Therefore, the conclusion that the yield value is independent of the fluidity of the oil seems justified; but, whereas this statement is probably true, there are factors which have not yet been considered which very greatly influence the yield value and therefore complicate the case. Thus, linseed oil paint has been used to compare with a blown linseed oil paint on the general assumption that they would be more nearly alike than would blown oil and mineral oil. But it is noted that 35 per cent lithopone in mineral oil with 2 per cent oleic acid gave a yield value of 115 and in a mixture of mineral and linseed oil a yield value of 40, although the fluidities of the three oils were not very different; hence, the chemical composition of the oil affects the yield value in a high degree. In the foregoing example equal *volume* compositions have been compared, but no new relationships are brought out.

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[5] THIS JOURNAL, **14**, 1014 (1922).

[6] Bingham, "Fluidity and Plasticity," p. 228.

The ratio between the mobilities of the acid-refined linseed oil paint and the blown linseed oil paint is 1.40:0.02 = 70, whereas the ratio between the fluidities of the oils is 2.42: 0.048 = 50. The two numbers are of the same order of magnitude, but the mobility of the blown oil paint is less than one would expect, for which no explanation has yet been found.

POLAR COLLOIDS IN SUSPENSION MEDIUM

Soaps are sometimes added to paints in order to give "false body." Just what they do is a matter of interest. The writers have experimented with zinc stearate and aluminium stearate.

When aluminium stearate is heated in linseed oil, it apparently dissolves but forms a stiff jelly or grease on cooling. The experiment was made of substituting part of the lithopone in a 55 per cent paint by weight with aluminium stearate up to nearly one per cent.

TABLE III—EFFECT OF ADDING ALUMINIUM STEARATE ON THE PLASTICITY OF A 55 PER CENT LITHOPONE IN ACID-REFINED LINSEED OIL PAINT

Aluminium Stearate Per cent	Mobility	Yield Value Observed	Yield Value Calculated
0	0.788 (B., B., and W.)	61.5(B., B., and W.)	61.5
0.25	0.679	250	249.5
0.65	0.697	550	550.3

The added material has produced a comparatively slight decrease in the mobility, but a very great increase in the yield value, which in the low concentrations is directly proportional to the concentrations. The last column in the table gives the values calculated by means of the linear formula

$$f = 752\, n + 61.5$$

DEFLOCCULATING AGENTS IN SUSPENSION MEDIUM

The attempt was made to grind 30 per cent by weight of lithopone in pure mineral oil. In spite of the low concentration of pigment, the grinding was very difficult, the paint being very pasty, and even after 48 hours of grinding measurements of the plasticity were difficult to make. The mobility was not peculiar, being about 1.0, but the yield value was extremely high—approximately 1090. But on adding as little as 0.2 per cent of oleic acid the yield value was reduced by 81 per cent, and 2.0 per cent reduced the yield value to a negligible quantity. During this extraordinary change in the yield value the mobility remained the same to within the experimental error.

It was proved by means of the microscope that the action of the oleic acid was one of deflocculation. It was also proved that the action was not due to the oleic acid acting as an electrolyte, for turpentine, which is a nonelectrolyte, has a very pronounced effect as a deflocculating agent, 1.5 per cent of it reducing the yield value to the extent of 92 per cent, and 3.0 per cent to a negligible quantity.

Stearic acid thinned down a paint, evidently lowering the yield value, but difficulty was encountered in getting consistent measurements. It would be worth while to prepare paints with a much higher yield value, in order to ascertain whether higher concentrations of the deflocculating agent than are required to furnish a layer one molecule deep over the particles would be effective in lowering the yield value.

That a 50 per cent mixture of linseed oil with mineral oil gave a yield value in a 65 per cent paint by weight of 970 as compared with 128.9 in straight linseed oil, points to the conclusion that even 50 per cent of linseed oil is not sufficient to completely disperse the pigment. The linseed oil had an acid number of 0.88.

MOISTURE

It is well known that moisture in a paint has important effects on its plasticity, but apparently no one has attempted to measure these effects quantitatively. Paint C, made up to contain 60 per cent by weight of air-dried lithopone in acid-refined linseed oil, was found to have a yield value of 90 and a mobility of 0.64 after 32 hours of grinding. On adding 0.5 per cent of moisture and grinding in the ball mill, it was found that the yield value had risen to the extraordinary value of 3450 dynes per sq. cm. and the mobility had fallen to 0.142 absolute unit. In thus affecting both the yield value and the mobility, moisture seems to play a unique role most nearly resembling the action of a polar colloid. A further study is planned to find out the effect on plasticity of both smaller and larger quantities of moisture, and to determine the mechanism of the phenomenon.

OXIDATION OR POLYMERIZATION

From experiments with lithopone in acid-refined linseed oil and in blown oil, it may be stated with some confidence that the yield value will not be altered except as the adhesion between the oil and pigment is changed, but that the mobility will be changed in direct proportion to the change in the fluidity of the medium.

In the grinding experiments it was observed that the mobility fell off with long continued grinding. It appears possible that there may be two counter effects—one due to the gradual wetting and separation of the individual particles, and the other due to the oxidation or polymerization of the medium. The latter tendency would adequately explain the falling off of the mobility on long grinding while the yield value remains constant. It was thought that this could be best tested by carrying out the grinding in a more inert atmosphere, using nitrogen or carbon dioxide.

In Table I the plasticity of a 60 per cent lithopone paint in acid-refined linseed oil, ground in atmospheric air, has already been given, this being Paint C. In Table IV are given the data of Paints D and N, the first being ground in an atmosphere of carbon dioxide, and the second being ground in an atmosphere of nitrogen with 0.5 gram of anticatalyst. Otherwise, the three paints are intended to be identical.

In each case the mobility at first increases, passes through a maximum, and then falls off more and more rapidly. The maximum occurs after about 32 hours' grinding, the value of the maximum being 0.63 for Paint C, 0.64 for Paint D, and 0.60 for Paint N. At the end of 64 hours the mobility of Paint C has fallen off probably 15 per cent, Paint D in carbon dioxide some 7 per cent, and Paint N in nitrogen some 6 per cent. Thus, it does not appear that an inert atmosphere is able to prevent the change which causes the falling off in the mobility.

It may be that still other factors than oxidation and polymmerization will eventually have to come in for study. The writers suggest the possibility of moisture derived from the pigment or the atmosphere, solid material resulting from the wear of the mill, alkaline material derived from the mill, or chemical reaction between the pigment and some part of the oil.

DISSOLVED GASES

In the course of this work it was observed that carbon dioxide is very soluble in paint. The writers have evacuated each paint before measurement so that they would be fully comparable. Assuming oxidation or polymerization to be the only change taking place on grinding, they expected the yield value to be the same in the three paints. They were therefore surprised to find the yield value quite different in the three paints—viz., 90 in Paint C, 280 in Paint D, and 200 in Paint N. Sufficient work has not been done as yet to make it safe to hazard an explanation of this striking difference. In these experiments the materials were used in their air-dry condition, but in future experiments it will be desirable to regulate the moisture conditions much more carefully.

TEMPERATURE

Work already done has made it appear that the increase in mobility with the temperature is in direct ratio to the increase in the fluidity of the medium. Naturally, this generalization is subject to limitations, since the adhesion may change with the temperature, colloids may pass from the gel to the sol condition as the temperature is raised, etc.

DIMENSIONS OF THE INSTRUMENT

All the measurements described in this paper were made on a given type of plastometer, for which changes in the length and radius of the capillary are without effect.

TABLE IV—CHANGE IN PLASTICITY DURING THE PROCESS OF GRINDING A PAINT

Time of Grinding Hours	Mobility in Absolute Units	Yield Value in Dynes per Sq. Cm.
Paint D, 60 per cent lithopone and 40 per cent acid-refined linseed oil, density × 1.742, temperature 25° C., capillary No. 10. Ground in an atmosphere of carbon dioxide		
16	0.61	340
24	0.61	280
32	0.63	280
49	0.64	280
56	0.62	270
64	0.61	280
Paint N, 60 per cent lithopone and 40 per cent acid-refined linseed oil, density × 1.747, temperature 25° C., capillary No. 10. Ground in an atmosphere of nitrogen		
6	0.51	310
22	0.58	230
34	0.59	210
40	0.60	200
48	0.57	150
52	0.57	95
56	0.55	100
70	0.56	150
80	0.53	110

CONCLUSIONS

1—As the grinding of a pigment in oil progresses, the yield value at first decreases but after 30 hours becomes constant. The mobility under the same conditions at first increases, passes through a maximum, and then decreases more and more rapidly. The maximum occurs after about 30 hours in these experiments.

2—On measuring different concentrations of pigment suspended in oil, the yield value–weight concentration curve is found to be linear except at low concentrations, thus confirming the findings of Bingham, Bruce, and Wolbach. All concentrations exhibit a yield value. The concentration of zero yield value is apparently independent of the nature of the medium.

The mobility–weight concentration curve is also linear and the concentration of zero mobility is apparently independent of the nature of the vehicle. The theory would lead one to expect that simpler relations would be found when using volume concentrations, but this is not the case, for which no explanation has yet been given.

3—Silica and lithopone have very different plasticity at the same weight concentration. When they are compared at equivalent volume percentages, however, the mobilities are nearly the same and the yield values are not very different. This fact is the more striking since the particle size in the two pigments is so different.

4—Comparing blown oil with acid-refined linseed oil at the same concentration of pigment, the effect of the fluidity of the medium is shown. The mobility falls off in presumably the same ratio as the fluidities of the oil, but the yield value is independent of the fluidity of the oil.

5—Polar colloids—as, for example, aluminium stearate—have very slight influence on the mobility, but they have an extraordinary effect in raising the yield value.

6—It is difficult to grind a pigment into pure mineral oil having the same fluidity as linseed oil and it is still more difficult to make a satisfactory plasticity determination on the resulting suspension. However, 0.2 per cent of oleic acid deflocculates the suspension and lowers the yield value about 80 per cent, while the mobility remains unchanged.

7—Moisture exerts a prodigious effect on the plasticity of paint, 0.5 per cent of moisture raising the yield value from 90 to 3450, and at the same time reducing the mobility to one-fourth of its former value.

8—Oxidation and polymerization affect the fluidity of an oil, so we should expect the mobility to be affected. It was thought that the fall in the mobility on long grinding might be attributable to one of these causes, but grinding in an atmosphere of nitrogen only prevented it, partially. A paint ground in an atmosphere of carbon dioxide has a yield value three times as high as when ground in the air.

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Oxygen and Oxygenated Air in Metallurgical Processes

Revolutionary changes in the metallurgy of iron, by which production costs should be materially decreased and quantities of low-grade ore and smelting fuels now considered worthless be made available as the result of the use of oxygen and oxygenated air in blast furnace practice, are suggested in a report recently made to the Department of the Interior by a committee appointed by the Bureau of Mines to study the problem.

In the past it has been necessary in the production of 1 ton of pig iron to pass 3 tons of inert nitrogen through the blast furnace, resulting in serious heat and metal losses. The elimination of such losses by the substitution of oxygen, or a mixture of oxygen and air, has long been considered, but has not been put into practice on account of the inability to produce oxygen in quantities at sufficiently low cost to make such application industrially possible.

In view of the many recent developments in oxygen manufacture, and considering the increasing cost and decreasing quality of the nation's raw materials, the Bureau of Mines appointed an advisory committee, of which M. H. Roberts of New York is chairman, to study the problem of the application of oxygen or oxygenated air to metallurgical and allied processes. This committee has made a thorough survey of the existing processes for the manufacture of 99 per cent oxygen, and finds that the oxygen industry is now able to make plants for supplying large quantities of oxygen to metallurgical industries at low cost.

The data collected by this committee indicate that the production and utilization of cheap oxygen should also accomplish great economies in the metallurgy of zinc. It is believed that similar economies can be effected in the metallurgy of copper, and in fact in all branches of nonferrous metallurgy.

The committee has developed plans for experimentally determining the effects of oxygen-enriched air upon the operation of the blast furnace, and it is recommended that these plans be put into effect as the first step of an extended research as to the general applicability of oxygen to metallurgy. The knowledge that German industrial concerns are working actively on the application of oxygenated air to metallurgical processes has greatly concerned American iron and steel interests, and the industry is making insistent demands for research work of this nature.

Insoluble Phosphoric Acid in Acid Phosphates and Fertilizers[1]

Some Sources of Error in Its Determination

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It is important to observe the precaution of washing the sample with water up to the volume of 250 cc. as prescribed in the official method, and also to select rapid filtering funnels so that the washing may be done in about 20 to 30 minutes.

There is an important relation between the Fe_2O_3 and P_2O_5 removed by thorough washing—as the percentage of Fe_2O_3 removed by washing is increased the percentage of insoluble P_2O_5 decreases.

While the same care should be exercised in making the ammonium citrate exactly neutral, as prescribed by the official method, yet moderate differences in the ratio of ammonia to citric acid make relatively little difference in the results for insoluble as compared to the importance of careful preliminary washing.

THE purpose of this article is to emphasize certain sources of discrepancies in the determination of insoluble P_2O_5, particularly those arising from incomplete preliminary washing of the sample, and the relative effect of using various solutions of ammonium citrate solution.

The official method of the Association of Official Agricultural Chemists prescribes: "Place 2 grams of the sample on a 9-cm. filter, wash with successive small portions of water, allowing each to pass through before adding more, until the filtrate measures about 250 cc. ***." This precaution of washing the sample to 250 cc. has not been observed by some analysts, resulting in many cases in wide discrepancies.

In the case of one sample of acid phosphate made from Tennessee phosphate rock, on which considerable collaborative analytical work was done, the importance of thorough preliminary washing was strongly emphasized. One group of analysts, accustomed largely to handling acid phosphate made from Florida rock, reported consistently about 0.75 per cent insoluble P_2O_5, while others, more familiar with acid phosphate made from Tennessee rock, found about 0.40 per cent insoluble. After a careful investigation, including exchange of samples of ammonium citrate, etc., it was developed that the trouble was entirely in the preliminary washing. Those who were in the habit of washing the sample at first with only three or four washings with water reported the highest results. After this investigation further determinations were made on the same sample, with a close agreement averaging, for ten analysts, 0.36 per cent, six of the number reporting 0.37 per cent. This work led to the following:

Sample A—Acid phosphate, after different periods of curing made from Tennessee rock (rock containing about 2.4 per cent Al_2O_3 and 2.7 per cent Fe_2O_3)

Period of Curing		PER CENT INSOLUBLE P_2O_5 Washed to 100 Cc. (4 to 5 Washings)	PER CENT INSOLUBLE P_2O_5 Washed to 250 Cc. (10 Washings)
1	day	2.19	1.96
10		0.94	0.62
4	weeks	0.48	0.35
6		0.49	0.31
10		0.50	0.38
12		0.65	0.45
14		0.48	0.33

Sample B—Acid phosphate, 6 months old, varied size of filter papers, also volume of water in washing (prior to treatment with ammonium citrate)

Volume of Washing Cc.	PER CENT INSOLUBLE P_2O_5 11-Cm. Filter	PER CENT INSOLUBLE P_2O_5 9-Cm. Filter
100	0.30	0.27
150	0.25	0.15
200	0.15	0.15
250	0.15	0.15

Sample tested directly, no preliminary washing with water—0.30 per cent insoluble.

Separate portions of Sample B were similarly washed, as above, and the Fe_2O_3 remaining in the washed residue determined.

	Per cent Fe_2O_3
Unwashed sample	2.35
After washing to 100 cc., 9-cm. filter	2.30
After washing to 150 cc., 11-cm. filter	2.30
After washing to 200 cc., 9-cm. filter	2.10
After washing to 250 cc., 9-cm. filter	2.05

Many analysts prefer the 11-cm. filter to avoid loss in washing when churning up the sample with the stream of water. There is apparently an advantage, in the case of some samples, in using a 9-cm. filter, since a greater number of washings is required to give the 250 cc. than when the 11-cm. filter is used. In most cases, however, ten washings on a 11-cm. filter using about 25 cc. each time were sufficient.

It has been found with some samples that the percentage of insoluble after washing to 250 cc. is quite appreciably lower than when washing to 150 cc. There seems to be an important relation between such results and the Fe_2O_3—the greater the number of washings the more Fe_2O_3 combined with P_2O_5 is washed through resulting in lower results for insoluble.

Several samples of acid phosphate were next taken, washed to different volumes, and the percentage insoluble P_2O_5 and Fe_2O_3 determined.

	Unwashed	PER CENT INSOLUBLE 100 Cc. (4 Washings)	PER CENT INSOLUBLE 150 Cc. (6 Washings)	PER CENT INSOLUBLE 200 Cc. (8 Washings)	PER CENT INSOLUBLE 250 Cc. (10 Washings)
Sample C—Acid phosphate 1 day old (Tennessee rock)					
P_2O_5	2.26	2.19	2.15	2.05	1.96
Fe_2O_3 in washed residue	2.05	2.00	2.00	1.90	1.80
Fe_2O_3 after citrate treatment	..	0.40	0.40	0.40	0.25
Sample D—Acid phosphate, 8 months old (Tennessee rock)[a]					
P_2O_5	0.32	0.29	0.20	0.14	0.12
Fe_2O_3 in washed residue	2.10	2.10	2.00	1.90	1.83
Fe_2O_3 after citrate treatment	0.43	0.40	0.38	0.35	0.28
Sample E—Double superphosphate (45 per cent available P_2O_5)[a]					
P_2O_5	..	2.40	2.25	..	2.14
Fe_2O_3 in washed residue	..	1.50	1.40	..	1.20
Sample F—Acid phosphate, 1 year old (Florida rock)					
P_2O_5	..	0.24	0.18	..	0.14
Fe_2O_3 in washed residue	..	1.20	1.10	..	1.06
Sample G—Acid phosphate, 1 week old (Florida rock)					
P_2O_5	..	0.55	0.42	..	0.38
Sample H					
Average results for insoluble P_2O_5 on eight samples of mixed fertilizers, containing acid phosphate, nitrogen, and potash	..	2.03	1.98	1.90	1.83

[a] The results in Samples D and E are the average reported by ten laboratories.

The importance of thorough washing of the sample with water prior to its treatment with ammonium citrate having been established, a series of tests was made to determine the effect of different solutions of ammonium citrate. Just prior to this, however, two samples of acid phosphate had been sent to twelve laboratories together with some of a solution of neutral ammonium citrate, with the request to determine insoluble P_2O_5 using this citrate solution and also using their own. The average of the twelve tests on the ammonium citrate solution sent from this laboratory showed a ratio of ammonia

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[1] Presented before the Division of Fertilizer Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922. Received August 17, 1923.

to citric acid of 1:3.759. The average results for insoluble from the twelve laboratories follow:

		Per cent Insoluble		
		Minimum	Maximum	Av.
	Sample I—Well-cured acid phosphate			
Citrate solution:	Other laboratories	0.08	0.29	0.18
	Author's laboratory	0.06	0.29	....
	Sample J—16 per cent acid phosphate			
Citrate solutions:	Other laboratories	0.73	0.95	0.88
	Author's laboratory	0.74	0.95	....

Nine laboratories reported results in close agreement on the first report, and after further work and observing the precautions of thorough preliminary washing, all agreed within 0.05 per cent. It was found that the difference was not due to ammonium citrate solutions, since the laboratory reporting the lowest results, likewise the one reporting the highest results, found the same with both solutions.

Per cent Insoluble

	Using Neutral Citrate Volume Preliminary Washing			Using Neutral Citrate Plus Ammonia or Citric Acid (Preliminary Washing 250 Cc.) Containing Excess Ammonia or Acid as Follows					
	100 Cc.	150 Cc.	250 Cc.		0.5%	1.0%	2.5%	5.0%	10.0%
Sample *K*—Mixed fertilizer, 2:10:10	1.20	1.12	1.09	NH_4OH	1.08	1.10	1.10	1.11	1.11
				Citric acid	1.08	1.02	1.00	0.95	0.95
Sample *L*—16% Acid phosphate from Florida rock	0.30	0.25	0.25	NH_4OH	0.25	0.25	0.17	0.16	0.16
				Citric acid	0.23	0.21	0.20	0.18	0.16
Sample *M*—Acid phosphate from Tennessee rock	0.37	0.30	0.25	NH_4OH	0.37	0.27	0.27	0.28	0.27
				Citric acid	0.25	0.20	0.15	0.14	0.12
Sample *N*—16% Acid phosphate plus lime	3.77	3.65	3.61	NH_4OH	3.62	3.62	3.67	3.97	4.12
				Citric acid	3.64	3.59	3.51	3.44	3.33
Sample *O*—Mixture acid phosphate and cottonseed meal	....	....	0.25	NH_4OH	....	....	0.23	0.25	....
				Citric acid	....	....	0.23	0.21	....

Sample K was then prepared and portions sent to ten laboratories. This was a sample of mixed fertilizer containing about 2 per cent NH_3, 10 per cent available P_2O_5, and 10 per cent K_2O. The results reported varied from 1.00 to 1.21 per cent, averaging 1.08 per cent.

In order to determine the effect of using a neutral solution of ammonium citrate as compared with solutions containing excess ammonia and others containing excess citric acid, the foregoing tests (Samples *K* to *O*) were made.

Similar tests were made on a mixture of equal parts of acid phosphate and bone meal, when the effect of adding ammonia or citric acid to a neutral solution of ammonium citrate was more marked.

It was found important to select a long-stem (5 to 6 inches), 60-degree funnel for the preliminary washing, and with a carefully fitted paper the washing up to 250 cc. may be done in 20 to 30 minutes. It was further noted that when this precaution is not observed and an hour or more is required for washing, the results for insoluble are generally higher. (Some analysts add a little paper pulp or asbestos to increase rapidity of washing.)

Many other determinations were made by using different grades of filter papers, varying the temperature of the wash water, diluting before precipitation, etc., but none of these changes affected the results appreciably, especially as compared with the importance of thorough preliminary washing of the sample.

Acknowledgment

The author wishes to hereby express his thanks to H. C. Moore for many suggestions offered in this work, to those who have made many collaborative determinations, and his assistant, L. C. Smith, who has made a large number of careful determinations in the work.

An Improved Stopcock[1]

By P. H. Kollewyn

Martinez, Calif.

This little article is written to introduce to chemical engineers who have experienced trouble with leaking valves an improved stopcock which does not leak if properly handled. It has all the advantages of the regular stopcock, as easy adjustment, quick opening and closing, without the disadvantages of sticking and subsequent hammering or twisting off of the square top of the stem.

This stopcock was invented[2] as a result of trouble arising from the frequent replacements of valves in the acid lines of a California oil refinery. The first one was installed there in 1919 and is still in use. In Mexico this valve was used exclusively on all lines for corrosive liquids and also for steam and hot-oil lines.

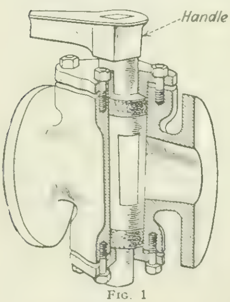

Fig. 1

The advantages of the double packed stopcock are:

Easy Installation—After the house is installed in the line the plug is put in and the top flange (see Figs. 1 and 2 showing the low- and high-pressure valves) is bolted on tightly, so tightly that the plug can hardly be moved. After this the bottom flange, which before installation was fastened snugly, is tightened, thus relieving the pressure on the plug which is taken up in the top and bottom packing. The bottom flange is tightened just enough to secure easy movement of the plug.

Easy Handling—In case the valve "sticks," due to wear, the top flange is slightly loosened and the bottom flange tightened, thus securing a very quick repair without danger of the operator breaking the stem or the house, because no force is used as hammering or twisting. This valve can be repaired without interfering with the operation.

Easy Cleaning—The two openings on both sides of the house make an effective cleaning possible without taking the valve out of the line.

Replacements of Parts—If, after long service, the plug is worn out too far, it can be easily replaced by an oversize or new plug, which means a considerable cut in costs because the housing remains in the line. The high pressure valve is very well adapted for a boiler blowoff valve. It carries an extra safety flange on top and if fitted with a diamond boring it complies with the government specifications, as it cannot be opened at once to its full extent because the plug and the house have to warm up slowly to the same temperature before the plug can be turned easily.

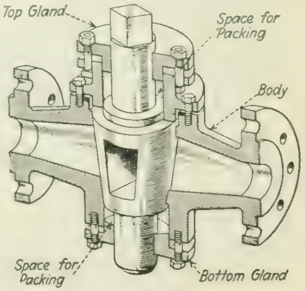

Fig. 2

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[1] Received May 2, 1923.

[2] U. S. Patent 1,370,745 (March 7, 1921).

Chemical, Physical, and Biological Properties of Bordeaux Mixtures[1]

By O. Butler

New Hampshire Agricultural Experiment Station, Durham, N. H.

In this paper it is shown that in practice three types of Bordeaux mixture are recognized—acid, neutral, and alkaline washes. The methods of preparation and chemical properties of these mixtures are briefly described and it is pointed out that as the lime content in a mixture is increased the shading action of the wash becomes more obvious and its adhesiveness increased until the ratio of cupric sulfate to calcium oxide exceeds 1:0.5 when it begins to fall. It is also shown that the rate of settlement of a Bordeaux mixture, on which much emphasis has been placed, is not in any sense a measure of adhesiveness. From the facts presented it could also be concluded that if the shadow cast by an alkaline Bordeaux mixture was injurious then a neutral mixture could be substituted and this depressing effect removed. It is also briefly pointed out that when Bordeaux mixtures are injurious at the time of application the injury produced depends both on the composition of the wash and the specific sensitivity of the organ sprayed.

LONG before the downy mildew of the grape was known in Europe the grape growers would, as soon as the fruit began to mature, daub upon the vines bordering the highways and byways a mixture composed of milk of lime and copper sulfate, the object being to prevent pilfering. The downy mildew appeared in the Gironde in 1881 and Millardet[1] noticed, in the course of perambulations in the environs of Bordeaux in 1882, that the mixture the vineyardists were in the habit of daubing upon their grape vines with a small fagot broom distinctly preserved the treated plants from the ravages of the disease. The importance of this fact did not escape him. Millardet immediately began experimenting, and on April 1, 1885, reported the results of his experiments. The mixture he used had the composition[2]

Copper sulfate	5.71 parts
Quicklime	10.71 parts
Water to make	100 parts

and was therefore thick and heavy and not suited for use in sprayers. The formula necessarily needed modification and the Bordeaux mixture proposed in 1885 was soon replaced by more fluid washes, the most radical change introduced being in the amount of quicklime used. The ratio of cupric sulfate to quicklime, which in the original wash was 1:1.87, was changed by Millardet and Gayon[3] in 1887 to 1:0.3. These authors proposed for use in general practice a Bordeaux mixture of this composition containing 3 per cent cupric sulfate, and for trial similar mixtures containing 2 per cent and 1 per cent cupric sulfate, respectively. Further modifications of the original formula were introduced from time to time by various authors, and before the close of the 19th century there were recognized in the literature three types of Bordeaux mixture—acid Bordeaux mixture, neutral Bordeaux mixture, and alkaline Bordeaux mixture.

Acid Bordeaux mixture is, strictly speaking, a wash so made as to contain a small amount of soluble copper and give a faint acid reaction. In practice, however, the mixture is usually made by adding milk of lime to a solution of cupric sulfate until an alkaline reaction is obtained, when a small amount of cupric sulfate is added, 0.1 per cent in the case of a 1 per cent Bordeaux mixture, and 0.2 per cent in the case of a 2 per cent Bordeaux mixture. Obviously, as usually prepared, acid Bordeaux mixture will not give an acid reaction, or contain soluble copper.

Neutral Bordeaux mixture is made by adding milk of lime to a solution of cupric sulfate until no soluble copper can be detected by means of potassium ferrocyanide,[4] or, more commonly, by adding milk of lime until an alkaline reaction is obtained. A Bordeaux mixture in which the ratio of cupric sulfate to quicklime is 1:0.3 falls in this group.

Alkaline Bordeaux mixture is a wash containing cupric sulfate to quicklime in a ratio of not less than 1:0.5, though mixtures containing a ratio 1:3 and 1:5 have been recently introduced.[5] The alkaline Bordeaux mixture most commonly used in the United States is a wash containing cupric sulfate and quicklime in equal amounts.

The ratio cupric sulfate to quicklime used in preparing a Bordeaux mixture has an important effect on the chemical, physical, and biological properties of the wash—is, in fact, of more importance than is commonly supposed.

CHEMISTRY OF BORDEAUX MIXTURES

According to Millardet and Gayon,[6] Chester,[7] Fairchild,[8] and the majority of writers on the subject, the reaction that takes place when cupric sulfate and milk of lime or limewater are brought together results in the formation of cupric hydroxide and calcium sulfate, calcium hydrate being also present when the limewater or milk of lime is used in excess. Millardet and Gayon[3] did, however, observe that cupric sulfate and calcium oxide would combine in the ratio of 1:0.179, which is very nearly the ratio required for the formation of the basic sulfate $5CuO.SO_3$; and Fairchild expressed the opinion that basic sulfates are at first formed when milk of lime is slowly added to a solution of cupric sulfate.

Sostegni[9] studied the reactions involved in the preparation of Bordeaux mixture, and concluded that the copper precipitate was composed of cupric hydrate, basic cupric sulfate, and a double sulfate of lime and copper.

Vermorel and Dantony[10] state that the copper is precipitated in acid Bordeaux mixtures as basic sulfates, but that in alkaline washes cupric hydrate is almost exclusively formed when the milk is poured quickly into a solution of cupric sulfate and basic sulfates where it is added very slowly.

The most comprehensive study of Bordeaux mixture has been made by Pickering. According to this author[11] the following distinct basic salts may be formed when cupric sulfate is precipitated by calcium hydrate in the form of limewater: $4CuO.SO_3$; $5CuO.SO_3$; $10CuO.SO_3$; $10CuO.SO_3.3CaO$.

These CuO.3CaO basic sulfates, omitting CuO.3CaO, which is of no particular interest to the student of Bordeaux mixture, are formed when cupric sulfate and calcium hydrate are combined in the proper proportions to give the following ratios of cupric sulfate to calcic oxide: $4CuO.SO_3$, 1: 0.166; $5CuO.SO_3$, 1:0.181; $10CuO.SO_3$, 1:0.2; $10CuO.SO_3.CaO$, 1:0.269. The basic sulfates $4CuO.SO_3$ and $5CuO.SO_3$ are somewhat soluble in the mother liquor, the former to the extent of 1 part in 40,000, the latter to the extent of 1 to 2 parts per million. The other basic salts, however, are quite insoluble in the mother liquor, though, beginning with $10CuO.SO_3$, they dissolve with increasing readiness in saccharose.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[*] The numbers in the text refer to the bibliography at the end of the article.

When the basic sulfates are boiled, $10CuO.SO_3$ decomposes with formation of cupric oxide, but the other basic salts are not affected. None of the basic salts crystallize with age.

In practice the only basic sulfates that can be found in Bordeaux mixtures are $5CuO.SO_3$, $10CuO.SO_3$, and 10 $CuO.SO_3$, $3CaO$ either alone or mixed, according to Pickering, with a more highly basic salt the composition of which has not been determined, $4CuO.SO_3$ does not occur, since even in acid Bordeaux mixtures the ratio of cupric sulfate to quicklime will always be such that the lowest basic sulfate that could be formed would be $5CuO.SO_3$.

In neutral Bordeaux mixtures cupric oxide gradually forms on standing, but does not appear in mixtures in which the ratio of cupric sulfate to calcium oxide lies between 1:0.25 and 1:1. When, however, mixtures of these latter types are boiled, cupric oxide may or may not form, its appearance depending on the percentage strength in cupric sulfate of the mixture, as a study of Table I will show.[12]

Table I Effect of Boiling on the Development of Cupric Oxide in Bordeaux Mixtures

Strength of Mixture Per cent	Ratio $CuSO_4$:CaO	Cupric Oxide
2	1:1.00	Formed
2	1:0.50	
2	1:0.25	
1	1:1.00	
1	1:0.50	
1	1:0.25	
0.5	1:1.00	Not formed
0.5	1:0.50	
0.5	1:0.25	Formed
0.25	1:1.00	Not formed
0.125	1:1.00	

These data show that as soon as there is sufficient calcium hydrate in solution to give, on combining with the cupric sulfate, the basic sulfate $10CuO.SO_3.3CaO$ or $10CuO.SO_3$.-$3CaO$ admixed with higher basic salts, no cupric oxide forms on boiling the mixture.

When first prepared the Bordeaux mixtures encountered in practice form gelatinous precipitates, which are not usually stable and change more or less profoundly, depending on the temperature, the percentage strength in cupric sulfate, and the ratio cupric sulfate to calcium oxide used. In acid and neutral Bordeaux mixtures cupric oxide gradually forms and the precipitate becomes granular; in alkaline Bordeaux mixtures the gelatinous precipitate is usually replaced by spherocrystals. If one prepares a series of Bordeaux mixtures containing 0.125, 0.25, 0.50, 1, 2, 4, and 6 per cent cupric sulfate, in which the ratio of cupric sulfate to calcium oxide is 1:1, he will find that spherocrystals will appear in all the mixtures except the 0.125 per cent wash. Bordeaux mixtures in which the ratio of cupric sulfate to calcium oxide is 1:0.5 behave similarly to 1:1 mixtures. The 0.125 per cent mixture shows little or no change with age, while in the stronger mixtures blue spherocrystals, apparently similar to those occurring in the 1:1 mixtures, appear, but more slowly than in washes of the latter type. It was found that in alkaline Bordeaux mixture cupric oxide did not always form when the wash was boiled. There is no relation between the formation of cupric oxide and the development of spherocrystals on standing. It would appear that in Bordeaux mixtures the copper salt at first formed is not stable. In acid and neutral washes it changes gradually to cupric oxide; in the alkaline washes the change is to the formation of spherocrystals irrespective of the reaction given by the copper salt when the mixture is first made. These differences are due to the limited solubility of calcium hydrate. In strong Bordeaux mixtures the copper is precipitated in the same form, but if the calcium hydrate in the form of milk of lime is used in large excess the reaction will continue until equilibrium is reached.

The crystallization of Bordeaux mixtures may be prevented by the use of a small amount of saccharose. Kelhofer,[13] who first proposed the use of saccharose for this purpose, states that the amount required is determined by the ratio cupric sulfate to calcium oxide used. For a 1 per cent Bordeaux mixture 1:1 the amount required for 50 gallons is 2 ounces. Alkaline Bordeaux mixtures containing small amounts of saccharose remain gelatinous for a number of months, but eventually cuprous and cupric oxides form.

Adhesiveness of Bordeaux Mixtures

The adhesiveness of Bordeaux mixtures has been studied by several investigators,[14] and the subject is one of considerable practical importance.

Acid Bordeaux mixtures are less adhesive than neutral washes, and very alkaline washes are not as adhesive as mixtures in which the ratio of cupric sulfate to quicklime is 1:0.5. From the standpoint of adhesiveness there is no reason for increasing the lime content of a Bordeaux mixture beyond the amount required to give the ratio 1:0.5. The adhesiveness of a strictly neutral Bordeaux mixture prepared from limewater—that is, a mixture in which the ratio of cupric sulfate to calcium oxide is 1:0.2—is extremely poor since it is very highly gelatinous, so gelatinous that when it dries on a leaf the rate of drying of the surface exposed to the air is so much faster than that of the layer in contact with the leaf, that the tension produced causes the edges to curl to such an extent that the greater part of the mixture flakes off. A strictly neutral Bordeaux mixture is not serviceable in practice. In fact, it is rather doubtful whether any benefit is to be derived from using extremely gelatinous mixtures. What is needed is copper in a very fine state of division. For instance, if we study the rate of settlement of a 1 per cent Bordeaux mixture 1:1 made with water at 10° C., a very gelatinous mixture, with a similar mixture made with water at 30° C., a wash in which the copper is precipitated partly in granular form, we will find marked differences in their rates of settlement but no difference in their adhesiveness to Coleus leaves.

Table II—Effect of Temperature of Water Used on the Rate of Settlement and Adhesiveness of 1 Per cent Bordeaux Mixture 1:1

Mixture Made with	Relative Numbers			Adhesiveness
	1/2 Hr.	1 Hr.	2 Hrs.	10 = perfect
Water at 10° C.	6.5	22.5	66.0	7.1
Water at 30° C.	100.0	250.0	445.0	7.1

It has generally been assumed that the adhesiveness of a Bordeaux mixture was greater in slowly than in rapidly settling mixtures and better in freshly made than in mixtures that had been prepared for some time. The data in Table II show that too much importance should not be attached to the method of mixing, but, on the other hand, the opinion that a freshly made mixture is more adhesive than one that has been allowed to stand would seem to be sound in the case of Bordeaux mixtures that crystallize. The data in Table III show that a Bordeaux mixture in which the copper precipitate has assumed the crystalline form is much less adhesive than a freshly made wash.

Table III—Relative Adhesiveness of 1 Per cent Bordeaux Mixture 1:1 Freshly Made and Deteriorated[14]

	Adhesiveness, 10 = perfect
Copper precipitate gelatinous	6.7
Copper precipitate crystalline	4.7

BIOLOGICAL PROPERTIES

PHYSICAL EFFECTS—Bordeaux mixtures are, as a simple inspection of the dried washes would show, unequally transparent, the opacity increasing as the ratio of cupric sulfate to calcium oxide approaches unity. One would therefore expect that a plant sprayed with a neutral wash would respond somewhat differently than a plant sprayed with an alkaline mixture, and, effectively, as the data in Table IV show, we find that the sprayed plant develops normally on the one hand and slightly abnormally on the other.

TABLE IV—EFFECT OF SPRAYING WITH BORDEAUX MIXTURE AND MILK OF LIME ON DRY MATTER FORMED AND TRANSPIRATION PER GRAM DRY MATTER[16]

	Dry Weight			Transpiration per Gram Dry Matter		
	Sprayed with Bordeaux Mixture			Sprayed with Bordeaux Mixture		
VARIETY USED	1:1 G.	1: Alkaline G.	Not Sprayed G.	1:1 G.	1: Alkaline G.	Not Sprayed G.
Radish Early Scarlet Globe	0.74	0.95	0.66	27.80	25.20	24 20
	1.97	2.33	2.74	37.50	27.60	30.60
	2.67	3.10	2.92	40.73	32.39	34.84
AVERAGE...	1.79	2.12	2.10	35.34	28.39	29.88
Tomato Bonny Best	2.42	3.18	2.95	19.70	9.77	9.95
	7.59	8.47	8.43	23.82	21.83	22.06
AVERAGE...	5.00	5.82	5.69	21.76	15.80	16.00
Bean Dwarf Horticultural	3.28	3.41	3.68	20.20	18.20	18.70
	3.60	4.76	5.38	6.52	4.97	4.78
AVERAGE...	3.44	4.08	4.53	13.66	11.58	11.74

The literature is not in agreement in regard to the effect of Bordeaux mixtures on the rate of transpiration of sprayed plants, though the weight of the evidence indicates increased transpiration.[15] It has been observed by Daggar and Bonns[16] that spraying with Bordeaux mixture increases transpiration especially at night. The writer has observed that increased transpiration is noticeable especially under conditions favorable for radiation and that Bordeaux mixtures are opaque to the infra-red. We would therefore expect, other things being equal, sprayed plants to transpire more actively at night than nonsprayed plants. However, it should be noted that increased transpiration of sprayed plants at night does not of itself account for the effect of Bordeaux mixtures, because all Bordeaux mixtures cause increased transpiration to some degree but they do not all affect plants in a similar manner. The response of sprayed plants is to be attributed to difference in translucency of the mixtures to the solar spectrum. Schrander[17] was the first to advance the view that the action of Bordeaux mixture on plants was one of shade. Bordeaux mixtures, however, while not equally opaque to luminous radiations, do not show *inter se* quite so marked differences as the behavior of the sprayed plants indicates that they should. The response obtained is not due to shade, using the term in its ordinary acceptance, but to different degrees of athermancy of the washes to the spectrum. When the spectrum as a whole is considered 1 per cent, alkaline Bordeaux mixture is much more opaque than neutral Bordeaux mixture, and there is concordance between the physical properties of the washes and the response of plants sprayed with them.

CHEMICAL EFFECTS—When we study the response of sprayed plants to the chemical action of Bordeaux mixtures we find rather a complex situation—we have to consider the effect of the mixture at the time of application, and the effect of the mixture after it has dried. The effect of Bordeaux mixtures after they have dried seems to be due entirely to the sensitiveness of the plant to soluble copper. The action of Bordeaux mixtures at the time of their application depends, on the other hand, on the type of mixture used, on the kind and variety of plant sprayed, and on the nature and age of the organ sprayed. In the *grape*, when Bordeaux mixtures are injurious it will be found that alkaline washes are more injurious than neutral mixtures, and that it is the young leaves that are damaged. In the *peach*, alkaline washes are more injurious to young than to old leaves, and neutral mixtures more injurious to old than young leaves. But, unlike the grape, the peach is sensitive to soluble copper and eventually the differences in behavior of the foliage following spraying are masked by copper injury. In the *tomato*, alkaline washes are more injurious than neutral Bordeaux mixtures, the injury due to alkalinity being noticeable on the young leaves. In the *apple*, neutral and alkaline Bordeaux mixtures of the usual types are injurious. The degree of alkalinity of the wash seems to have little or no influence on the intensity of the injury produced. However, the apple is somewhat sensitive to soluble copper and the fruit much more so than the foliage. In fact, the apple is so sensitive to soluble copper after the blossoms have fallen that Sanders and Brittain introduced Bordeaux mixtures in which the ratio of cupric sulfate to calcium oxide is 1:3 and 1:5 in order to reduce injury. Bordeaux mixtures of this type can be used on the apple very successfully, and cause very little if any injury. The reduction in the amount of the injury produced is not brought about, however, by any change in the nature of the copper precipitate formed, but by the fact that such a large excess of lime both delays and impedes carbonation and consequently the dissolution of the copper in meteoric water.

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Cellophane Plant under Construction

Cellophane, a transparent, cellulose product, used largely in millinery for decoration and in other trades for wrapping purposes, is to be manufactured by the du Pont Cellophane Co., a subsidiary of the E. I. du Pont de Nemours & Company. A plant to cost approximately $2,000,000 is now being constructed on the Niagara River at Buffalo, N. Y. This will be the first plant to manufacture this product in the United States. Cellophane has been produced in France for the past several years and its use is extending for wrapping purposes for confectionery, biscuits, cakes, tea, coffee, cocoa, meat products, and, in fact, for nearly all articles of food, as well as for perfumery, soap, various toilet preparations, pharmaceutical products, and others.

It is an important addition to the list of cellulose products produced by chemists for commercial uses during the last several years. It is nongelatinous, will not melt in boiling water, or decay. It is described as entirely harmless, water- and grease-proof, odorless, and can be dyed in any shade, printed or embossed, making it especially attractive as millinery decoration. It is manufactured in either sheets or rolls.

The du Pont Cellophane Company has obtained the patent rights for North America and pending the completion of its factory at Buffalo will be the selling agents in this country for the product. The company is now importing it. It is expected that the new factory will be completed in May or June of next year.

Analysis of Triphenylmethane and Azo Dyes by Titanous Chloride[1]

By W. S. Calcott and F. L. English

E. I du Pont de Nemours & Co., Wilmington, Del.

The titanous chloride titration has been applied in the determination of strength of commercial dyes of the triphenylmethane and azo classes, satisfactory results having been obtained in the routine analysis of about thirty representatives of the former and over a hundred of the latter. The method gives results accurate to about 0.5 per cent.

Although the application of titanous chloride to the analysis of dyes was introduced by Knecht and Hibbert about twenty years ago,[2] little seems to have been done in the commercial application of the method, in this country at least, until the last few years. This seems to be attributable chiefly to the long-standing prejudice, on the part of both dye manufacturers and consumers, against any form of chemical analysis of dyes, upon the ground that the only criterion of the value of a dye is the dye test. While this is undoubtedly true so far as shade, fastness to light and washing, brightness, etc., are concerned, sufficient data are now available to prove the superiority of the chemical method in the estimation of strength. In the standardization of dyes for the trade, the titanous chloride titration has therefore supplemented rather than superseded the dye test.

Perhaps an even greater service is rendered as a guide and control in the manufacturing processes. The lack of a rapid and accurate method for determining the purity of dyes has been a source of embarrassment in the synthetic work in both laboratory and plant. Heretofore, the dye test has been the basis for the estimation of yields, but this method alone is unsatisfactory for the purpose, not only because of the large variations frequently encountered between duplicate determinations upon the same sample, but also because the results must be expressed in terms of some arbitrary standard, the composition of which is usually unknown. The results of the titanous chloride titration, on the other hand, may be calculated upon the basis of either absolute purity or the standard dye, as desired.

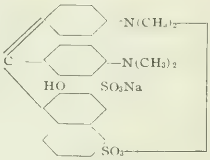
The determination of elemental constituents of the dye molecule, nitrogen, sulfur, etc., has been used to a slight extent, but little confidence can be placed in the results, since the impurities in the sample usually contain the element sought.

PREPARATION AND STANDARDIZATION OF SOLUTIONS

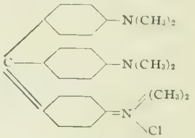
For all dye titrations a 0.05 *N* titanous chloride solution was used, the method of preparation, storage, and use having been previously described in detail.[3] Standardization was accomplished by means of Metanil Yellow purified as described later under the analysis of that compound. The procedure consisted in dissolving about 0.20 gram of the dye in 50 cc. of water and 50 cc. of 25 per cent sodium tartrate solution, boiling to expel air, and titrating the hot solution to a colorless end point in an atmosphere of carbon dioxide. Triplicate titrations should agree within 0.2 per cent in the normality factor.

TRIPHENYLMETHANE DYES

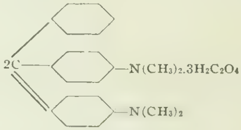
Three representatives of this class, Pontacyl Green S, Crystal Violet and Victoria Green, were studied, their titration presenting no difficulty.



PONTACYL GREEN S



CRYSTAL VIOLET



VICTORIA GREEN

The reaction consists in the reduction of the dye to its leuco base with the consumption of two atoms of hydrogen, the analytical procedure being as follows:

> Dissolve the sample (equivalent to 30 to 50 cc. of 0.05 *N* titanous chloride) in a mixture of 50 cc. of water and 50 cc. of alcohol[4] in a 300-cc. Erlenmeyer flask. Add 50 cc. of 25 per cent sodium tartrate solution, boil 3 to 5 minutes, admit a rapid stream of carbon dioxide, and titrate the hot solution with 0.05 *N* titanous chloride to the last distinct color change, passing carbon dioxide throughout the titration. With average dye samples the end points are sharp, being determinable within two to four drops of titanous chloride.

The samples upon which the experimental work was done were purified by repeated crystallizations from water and alcohol, the purity of the final product being checked by nitrogen, sulfur, or chlorine determinations.

Wide variations were made in the conditions of the analysis, the results obtained upon Pontacyl Green S, set forth in the following tables, being typical of the other dyes studied and proving the titration to be independent of reasonable variations in procedure.

TABLE I -EFFECT OF CONCENTRATION OF SODIUM TARTRATE
(Assay = 0.3049 gram, 1 cc. $TiCl_3$ = 0.01219 gram dye)

No.	25% Sodium Tartrate Cc.	$TiCl_3$ Cc.	Purity %
1	5	No end point	...
2	10	About 25	...
3	18	24.05	96.20
4	20	24.08	96.32
5	25	24.05	96.20
6	50	24.10	96.40

In these experiments, one-half the proper size sample was used because of the small amount of purified material available. In Nos. 1 and 2, the color of the solution at the end of the titration was red and the end point indistinct. The fact that 18 cc. of the 25 per cent tartrate ($Na_2C_4H_4O_6.2H_2O$) are equivalent to the free hydrochloric acid in 25 cc. of the titanous chloride solution indicates that free mineral acid is detrimental, but in addition to this buffer action the tartrate has a specific effect since titrations in the presence of an equivalent amount of sodium acetate were unsuccessful.

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[1] Presented before the Division of Dye Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Ber.*, **36**, 166, 1549 (1903); **38**, 3318 (1905); **40**, 3819 (1907); "New Reduction Methods in Volumetric Analysis," Longmans, Green & Co., **1910**, reprinted with additions in **1918**.

[3] THIS JOURNAL, **12**, 994 (1920).

[4] Alcohol denatured with benzene is satisfactory.

TABLE II—EFFECT OF TEMPERATURE OF TITRATION

(Assay = 0.3049 gram, 1 cc. $TiCl_3$ = 0.01219 gram dye)

No.	Temp. ° C.	$TiCl_3$ Cc.	Purity %
1	50	24.06	96.24
2	60	24.03	96.12
3	70	24.07	96.28
4	Boiling	24.05	96.20

The temperature of titration is thus seen to have no appreciable effect upon the reaction.

TABLE III—EFFECT OF VARIATION IN ALCOHOL

(Assay = 0.3049 gram, 1 cc. $TiCl_3$ = 0.01219 gram dye)

No.	Alcohol Cc.	$TiCl_3$ Cc.	Purity %
1	..	23.81	95.24
2	15	23.93	95.72
3	25	24.12	96.48
4	50	24.10	96.40

In Nos. 1 and 2 the sample was not in complete solution. The concordant results of Nos. 3 and 4 indicate that alcohol, in excess of a certain necessary minimum, has no effect.

The following analyses were made upon material that had been crystallized three times:

TABLE IV—ANALYSIS OF PURE PONTACYL GREEN S

(Assay = 0.6097 gram, 1 cc. $TiCl_3$ = 0.01219 gram dye)

No.	$TiCl_3$ Cc.	Purity %
1	49.85	99.70
2	49.92	99.84
3	49.89	99.78
4	49.97	99.94
5	50.03	100.06
6	49.90	99.80
	Average	99.85

Crystal Violet behaved in all respects like Pontacyl Green S, but in the analysis of Victoria Green a little difficulty was encountered due to the variable composition of the dye samples. The formula for this dye given in the standard reference books shows the commercial article to contain two mols of dye base to three of oxalic acid, which would give an oxalic acid content of 29.1 per cent. When, however, pure material was prepared by repeatedly recrystallizing from 1 per cent aqueous oxalic acid solution and drying to constant weight *in vacuo* at 40° C., the product, when analyzed by the procedure found satisfactory for Pontacyl Green S, gave results varying from 103.2 to 104.4 per cent, calculated on the basis of the preceding formula. These high results cast suspicion upon the oxalic acid content, to confirm which oxalic acid determinations were made through the gravimetric calcium oxalate procedure. These showed the oxalic content of different samples to be quite variable, results between 23.0 and 26.3 per cent oxalic acid being obtained; the lower values were yielded by the samples crystallized from water and the higher by those from dilute oxalic acid. When this indefiniteness of constitution was taken into consideration, satisfactory analyses were obtained by the titration method, as indicated by the results set forth below, obtained upon samples crystallized from dilute oxalic acid.

TABLE V—COMPLETE ANALYSIS OF VICTORIA GREEN SAMPLES

CONSTITUENT DETERMINED	Sample A %	Sample B %
Dye by $TiCl_3$ (calcd. without $H_2C_2O_4$)	72.40	72.58
$H_2C_2O_4$	26.14	26.30
H_2O (50° C., *in vacuo*)	1.12	1.27
TOTAL	99.66	100.15

In addition to these three dyes studied in detail, the titration has been applied successfully in the routine laboratories to various other triphenylmethane colors.

AZO DYES

In attempting to apply the methods for the titration of azo dyes recommended by Knecht and Hibbert,[5] difficulty was frequently encountered in the high color of the reduced solution, which masked the end point of the titration. Investigation revealed the fact that this color depends to a large extent upon the nature of the medium in which the sample is dissolved, so that by a judicious choice of solvents the direct titration of a dye is made possible which otherwise would require the less convenient indirect method. Unfortunately, no means of predicting the required solvent mixture from the constitution of the sample has been established to date; consequently, in undertaking the analysis of a new dye, the medium must be determined by trial. On the other hand, the data acquired in the analysis of a large number of azo dyes show that any combination of the solvents experimented with which yields a sharp end point gives concordant results of sufficient accuracy for commercial purposes. It may also be stated that in all direct titrations of azo dyes the presence of sodium tartrate (or Rochelle Salt) is either absolutely necessary or highly advantageous and, conversely, in all back titrations excess of sodium tartrate must not be present since titanous chloride is decomposed upon boiling in the absence of free mineral acid.

From these considerations it is evident that no procedure of universal application can be given. The general outline of the methods employed is as follows:

DIRECT TITRATION—Dissolve the sample, which should be equivalent to 30 to 50 cc. of 0.05 *N* titanous chloride, in 50 to 100 cc. of an appropriate solvent (water, alcohol, acetic acid, or mixtures of these) in a 300-cc. Erlenmeyer flask, add 50 cc. of 25 per cent sodium tartrate solution, and boil for 3 to 5 minutes. Admit a rapid stream of carbon dioxide, connect the flask to the buret, and titrate the hot solution with 0.05 *N* titanous chloride to the last distinct color change. If the standard solution is added in 0.2-cc. portions toward the end of the titration, a satisfactory end point can be detected in even a quite highly colored solution.

INDIRECT TITRATION—Dissolve the sample (equivalent to about 30 cc. of titanous chloride solution) in 50 to 100 cc. of solvent, add 25 cc. of 40 per cent sulfuric acid or concentrated hydrochloric acid, boil to expel dissolved air, sweep with carbon dioxide, and add 50 cc. of 0.05 *N* titanous chloride solution. Boil 5 minutes and titrate the hot solution with 0.05 *N* ferric alum solution. It frequently happens that the reduction products of the dye serve as indicator, but if this is not the case 2 cc. of a 0.1 per cent solution of reduced Methylene Blue should be added previous to the back-titration. This indicator is prepared by dissolving 0.5 gram of dye in 100 cc. of 50 per cent alcohol and 50 cc. of 25 per cent sodium tartrate solution, titrating hot with titanous chloride to discharge off the blue color and diluting to 500 cc. The solution should be stored under carbon dioxide, as it is rapidly reoxidized by air.

Either method is rapid, the direct titration requiring 15 to 20 minutes and the back titration but little longer, and the results by either, when applied to average samples, should be reproducible within about 0.5 per cent. In the analysis of dye mixtures, the results cannot be calculated upon the absolute basis of the Metanil Yellow standardization, but must be expressed in terms of a standard dye known to contain the same ingredients as the sample in approximately the same ratio.

In all cases the samples dealt with were purified by recrystallization from water or mixtures of alcohol and water, and the purity of the final product was checked by elementary analysis. Since Metanil Yellow was used as the ultimate standard, especial care was exercised in its purification,

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[5] "New Reduction Methods in Volumetric Analysis," 1918, p. 76.

TABLE VI —ANALYSIS OF AZO DYES BY TITANOUS CHLORIDE

DYE	Molecular Weight	COMPOSITION	Procedure	Normality of $TiCl_3$	Assay G.	Solvent Cc.	$TiCl_3$ Cc.	Iron Cc.	Purity by $TiCl_3$ %	Purity by Sulfur or Nitrogen %
Metanil Yellow	375.3	Metanilic acid + diphenylamine	..	.....	0.2000	....	46.85	...	100.04	......
			1	0.04897	0.2100	50 water	49.15	...	99.96	N, 99.8
			..	.....	0.2299	....	50.01	...	100.02	......
Orange II	350.2	Metanilic acid + ρ-naphthol	..	.....	0.2000	....	49.96	...	99.56	......
			1	0.04552	0.2000	50 water	50.06	...	99.76	......
Chrome Black 6B	394 3	1 2 4 acid + ρ naphthol	..	.....	0.2415	50 alcohol	49.50	...	99.00	......
			1	0.04897	0.2415	25 water	49.50	...	99.00	N, 98.5
			..	.....	0.2415	25 acetic	49.40	...	98.80	S, 99.3
Sky Blue 6B	992 7	Dianisidine + 2 Chicago acids	..	.....	0.2824	....	44.25	...	88.50	.....
			1	0.04552	0.2824	50 water	44.45	...	88.90	N, 88.5
			..	.....	0.2824	50 alcohol	44.40	...	88.80	S, 88.6
Basic Brown G	419.2	3-Phenylenediamine	..	.....	0.1259	....	50.00	12.20[a]	74.00	...
			2	0.04803	0.1259	100 water	50.00	12.20	74.00	N, 74.5
			..	.....	0.1259	....	50.00	12.00	74.40	......
Basic Brown B	461.3	3-Tolylenediamine	..	.....	0.1388	....	50.00	5.40[a]	87.40	..
			2	0.04803	0.1388	100 water	55.00	9.90	87.00	N, 87.6
			..	.....	0.1388	....	60.00	14.60	87.00	......
Chrysoidine R	262.7	Tolylenediamine + aniline	..	.....	0.1577	....	49.90	...	99.80	....
			1	0.04803	0.1577	50 water	49.85	...	99.70	N, 99.05
			..	.....	0.1577	25 acetic	49.92	...	99.84	......

[a] 1 cc. of iron solution = 1.062 cc. of $TiCl_3$.

the crystallizations—two from water and three from alcohol—being continued until the final crop of crystals and the material obtained upon concentration of the last mother liquor consumed identical percentage quantities of titanous chloride. The final product was dried to constant weight at 120° C.

In the foregoing table are summarized typical results obtained upon representative azo colors. In Column 4, the figures 1 and 2 refer, respectively, to the direct and indirect titration procedures.

BASIC BROWNS AND CHRYSOIDINES

In the analysis of the Basic Browns and Chrysoidines, a special procedure is necessitated by the instability of these compounds toward heat. In the former case, which is an indirect titration, the sample was dissolved, the flask swept with carbon dioxide, and the titanous chloride added at room temperature, after which the reaction mixture was boiled and the determination completed according to the usual procedure. With the Chrysoidines, titration was begun at 65° C., temperatures above 70° C. causing appreciable decomposition with consequent low results.

ADDITIONAL WORK

In addition to the dyes studied above in detail, the titration method has been successfully applied in the routine laboratories to the analysis of about twenty-five triphenylmethane and over a hundred azo colors.

Since the completion of this investigation, the titration of azo dyes with titanous chloride with electrometric determination of the end point has been described by Jones and Lee.[6] It is probable that such a procedure would overcome, to a considerable extent at least, the arbitrary effect of solvent upon the titration encountered in our work.

[6] THIS JOURNAL, **14**, 46 (1922).

Action of Barium Chloride on Sulfate in Fused Salts[1]

By Howard E. Batsford

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The action of barium chloride on sulfate in aqueous solution is so well known as not to need repetition, but whether this same action took place when in a mixture of fused salts, such as sodium and calcium chlorides, was an open question. Foote and Martin,[2] as a result of investigations on the action of barium chloride in fused mercuric chloride, found that the chlorides of most of the divalent metals were not soluble in mercuric chloride. However, this work, though of a similar nature to that undertaken by the writer, was not conclusive evidence that the reaction $BaCl_2 + R_2SO_4 = BaSO_4 + 2RCl$ would occur in quantitative amount in other fused salts.

In connection with the electrolysis of fused salts it is very desirable to obtain as pure salt as possible, in order to prevent irregularities in the electrolytic action. The usual practice is to purify the salts in aqueous solution, then to dehydrate them thoroughly and proceed to fuse them for manufacture of the respective metals.

An effort was made to study the effect on electrolysis of adding slightly impure or commercial salts to the fused cell. The result was a lowering of the current yield coupled with foaming of the bath and disturbed thermal relations. It was found that barium chloride added from time to time had an accelerating action on the metal production, but to what this action was attributable was unknown. The questions naturally arose, whether barium chloride affected the cell by reaction with the sulfate impurities, and what effect it had on the fusion point when added in small quantities to the melt.

The second question was settled definitely in a short time by making up known mixtures of sodium and calcium chloride, analyzing them, and running them for freezing points, then repeating the operation with samples containing varying small quantities of the barium salt (Fig. 1).

The experiment on the action of barium chloride on the sulfate occupied several days. During the regular operation of the electrolytic cell barium chloride was added hourly in known amounts, samples of the molten electrolyte and bottom sludge being taken at proper intervals.

Analyses were made of all materials entering and leaving the furnace, as well as of the material remaining at the end of the run. On account of the length of each run and the large quantities of electrolyte employed, the chance of large percentage loss was remote.

It was found that (1) barium chloride did not change the freezing point when added in small quantities; (2) barium chloride in molten salt mixtures acted as a purgative, precipitating quantitatively the sulfate existing as impurity in the salts.

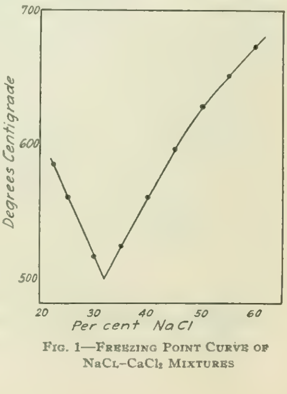

FIG. 1—FREEZING POINT CURVE OF NaCl–$CaCl_2$ MIXTURES

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[1] Received May 21, 1923.

[2] *Am. Chem. J.*, **41**, 451 (1909).

A Method for the Determination of Tolidine[1,2]

By S. Palkin

Color Laboratory, Bureau of Chemistry, Washington, D. C

THE determination of tolidine by nitrite titration[3] has an apparent advantage in that it is comparable to the process involved when the base is to be used for tetrazo dyes. This method is, however, subject to the usual difficulties incident to diazotization, such as uncertainty of end point with starch iodide indicator, as well as instability of the product formed. The reaction is, moreover, a time reaction, requiring periodic standing and observations, to approximate completion of the diazotization. An iodometric method[4] described by Roesler and Glasmann has similar disadvantages and depends upon spot tests for determination of the end point. Both methods, while simple, require considerable skill and practice before any degree of accuracy can be approximated.

It is well known that tolidine and benzidine form a number of very difficultly soluble salts, and advantage has been taken by Raschig[5] and others[6] to make use of the sulfates of these bases for determination of the sulfate radical. No method which makes use of this property of tolidine for the determination of the base itself, however, has been found on record. The Raschig[5] method requires an excess of tolidine to insure complete precipitation.

The method described in this paper makes use of the more soluble salt, the dihydrochloride of tolidine, and depends upon the fact that the dihydrochloride can be removed from aqueous solution by the introduction of saturated salt solution. The tolidine dihydrochloride, which is freed from excess hydrochloric acid and other impurities by washing with salt solution, can then be titrated acidimetrically, using a suitable indicator.

Description of Method

About 0.5 to 1 gram of sample is dissolved in dilute, 1 *N* hydrochloric acid solution, using heat. About 10 cc. of 3.5 per cent acid will be required per gram of tolidine. To the tolidine solution is then added a saturated sodium chloride solution, using about 100 cc. of saturated salt solution to every 10 cc. of tolidine solution. The tolidine dihydrochloride is allowed to crystallize out for about 20 or 30 minutes and is filtered by suction through a small 3 or 4-cm. paper on a perforated plate. The precipitate is washed several times with saturated salt solution to remove all free acid and other impurities.

The precipitate of tolidine dihydrochloride is then transferred completely to a 150-cc. beaker, paper and all, and dissolved in hot water to a clear solution. To this solution is added 0.1 *N* ammonium hydroxide solution slightly in excess, as determined by methyl red indicator. About 55 cc. of 0.1 *N* ammonium hydroxide per 0.5 gram of tolidine is a convenient amount. The precipitate of tolidine base is then allowed to stand a few minutes, filtered by suction, and washed with water. The excess ammonia is titrated back with 0.1 *N* hydrochloric acid solution, using methyl red as indicator, and the volume of ammonium hydroxide consumed is obtained by difference. One cubic centimeter of 0.1 *N* ammonium hydroxide equals 0.0106 gram of tolidine. Standard sodium or potassium hydroxide may be used instead of ammonia, but the usual precaution to keep it free from carbonate must be taken.

Using this method in a series of tests on specially purified tolidine with melting point 129° C., it was possible to account for 99.82 per cent in an average of nine determinations. The minimum recovery in these experiments was 99.52 per cent, and the maximum recovery was 99.96 per cent. The recovery on a less pure sample of tolidine with melting point of about 128° C. showed variations of the same magnitude. These results are shown in Table I.

Table I—Application of Method

No.	Tolidine Taken Grams	Standard Alkali Consumed Cc.	—Tolidine Found— Grams	Per cent
1[a]	0.2500	22.95	0.2494	99.76
2	0.2500	22.95	0.2494	99.76
3	0.2500	22.9	0.2488	99.52
4	0.5000	46.0	0.4998	99.96
5	0.2500	23.0	0.2499	99.96
6	1.0000	91.9	0.9985	99.85
7	0.5000	45.9	0.4987	99.74
8	0.5000	45.95	0.4993	99.86
9	0.2500	23.0	0.2499	99.96
11[b]	1.0000	91.5	0.9941	99.41
12	0.7500	68.5	0.7443	99.2
13	0.1000	9.1	0.0989	98.9
14	0.0500	4.7	0.0510	102.0
15	1.0000	91.5	0 9941	99.41
16	1.0000	91.5	0.9941	99.41
17	0.5000	45.8	0.4976	99.52
18	0.2500	22 8	0.2477	99.08
19	0.1000	9.1	0.09887	99.87
20	0.0500	4.55	0 0494	98.86

[a] Nos. 1 to 9 obtained by further purification from *b*, melting point 129° C.

[b] Nos. 11 to 20 obtained by purification of technical tolidine.

Experiments were also conducted to determine whether the method was sensitive to variations in salt and acid concentrations. As shown in Table II, these two factors are without appreciable effect.

Table II—Effect of Variations in Hydrochloric Acid and Sodium Chloride Concentrations

No.	Tolidine Solution[a] Cc.	Salt Solution Used Cc.	HCl Added Cc.	Standard Alkali[b] Consumed Cc.	Tolidine Found Grams
21	5	50	..	22.6	0.2455
22	5	50	...	22.5	0.2445
23	5	50	0.1	22.5	0.2445
24	5	50	0.2	22.5	0.2445
25	5	50	0.5	22 6	0.2455
26	5	50	1.0	22.45	0.2439
27	5	50	2 0	22.8	0.2477
28	5	50	3 0	22.55	0.2450
29	5	50	4.0	22.6	0.2455
30	5	50	5 0	22.65	0.2461
31	5	50	. .	22.5	0.2445
32	5	50		22.8	0.2477
33	5	50	.	22.55	0.2450
34	5	50	.	22.65	0.2460
35	5	40		22.45	0.2439
36	5	40	.	22.45	0.2439
37	10	90	...	45.1	0.4900
38	10	100		45.2	0.4911
39	10	80	. .	45 2	0.4911
40	10	100	...	45.3	0.4921

[a] Approximately 10 grams tolidine and 12 cc. concentrated hydrochloric acid dissolved in 200 cc. water. 1 cc. contains approximately 50 mg. tolidine.

[b] NH_4OH solution used was 0.10245 *N*.

Note: Probable error in pipetting tolidine solution = 1 drop (0.05 cc.) which is 50 × 0.05 = 2.5 mg.

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[1] Presented before the Division of Dye Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Contribution No. 78 from the Color Laboratory, Bureau of Chemistry, Washington, D. C.

[3] Cain and Thorpe, "Synthetic Dyestuffs and Intermediate Products," **1918**, p. 312.

[4] *Chem. Ztg.*, **27**, 986 (1903).

[5] *Z. angew. Chem.*, **26**, 617 (1903).

[6] Müller and Dürkes, *Z. anal. Chem.*, **47**, 477, 653 (1903).

Some Simplified Routine Tests in Sugar-Mill Laboratories[1]

By K. R. Lindfors

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Every beet-sugarhouse chemist is familiar with the apparently endless stream of samples brought into the laboratory to be tested, also with the fact that the work must be performed to a great extent by benchmen with often no knowledge of analytical chemistry. Such conditions undoubtedly exist in the great majority of sugar mills, and in order to accomplish the work only methods of greatest speed and simplicity can be utilized. Therefore, modifications increasing the speed, or decreasing the chance of error, ought to be of interest to sugarhouse chemists.

The purpose of this paper is to call attention to a few simplified methods, little known, or such modifications thereof as have been found necessary in order to insure reliable results or lessen the work involved.

DETERMINATION OF SUGAR IN LIME CAKE

THE official method of decomposing the saccharate of lime present with acetic acid requires considerable time as the acid should be added very slowly in order to insure complete decomposition without excess. A modification involving the addition of a definite amount of acetic acid is sometimes used, but as the composition of the lime cake varies considerably from time to time, this amount may be either too large or too small. Ammonium nitrate has been substituted in many cases, but it is not only expensive, but rapidly corrodes the brass fittings on the polariscope tube.

Herles[2] recommends the use of ordinary neutral lead acetate for decomposition of the saccharate present. The lead acetate combines with the lime producing calcium acetate and hydroxide of lead, setting the sugar free.

As 2 molecules of lead acetate combine with 1 molecule of calcium oxide, 1 gram of lime will require 13.54 grams of lead acetate. Lime cake ordinarily does not contain more than 4 per cent of caustic lime; 14.11 grams of the reagent will therefore be sufficient for normal weight of the cake.

Furthermore, as about 5 cc. of insoluble matter are present in 26 grams of cake, it becomes necessary to fill up to 105 cc. in order to get a direct percentage of sugar. Hence, the total volume to be added is 86.98 cc. which must contain 16.22 grams of the acetate. But as an excess does no harm, it is recommended to use 20 grams of lead acetate per 100 cc. of water. The advantage of this reagent lies in the fact that it not only decomposes the saccharate present, but at the same time precipitates the impurities, as the hydroxide formed during decomposition combines with the excess of the reagent to basic acetate of lead.

Usually, there are no 105-cc. flasks available. Herles, therefore, recommends the following modification of his method:

> Weigh out 30 grams of lime cake, add with a pipet 100 cc. of the lead acetate solution, mix, filter, and polarize. If the weighing is done in a dish with a tight fitting cover in which is placed a piece of a suitable brass chain, a few moments of violent shaking will accomplish the mixing of the reagent and the lime cake.

The method gives very good results in straight sugar mills, but when the Steffen process is used the amount of caustic lime present is sometimes considerably greater; therefore, the amount of lead acetate added according to the foregoing directions is not sufficient to complete the decomposition of the saccharates. The difficulty was finally overcome by the use of 25 grams of lead acetate per 100 cc. (in place of 20 grams) and the addition of 1 to 2 cc. of concentrated or glacial acetic acid per liter, the amount of acetic acid to be added depending upon the presence of carbonate of lead in the commercial product. In straight houses sufficient acetic acid to insure a perfectly clear solution was used, and in Steffen's, 1 to 2 cc. additional.

STEFFEN'S WASTE AND WASH WATERS—As neutral or slightly acidulated lead acetate so effectively broke up the saccharate present in lime cake, its use for similar purpose in other materials containing bound sugar was naturally suggested. It was therefore tried in place of acetic acid on Steffen's waste and wash waters. The result was very satisfactory. A large number of experiments were made, with good checks, and finally this procedure was adopted:

> With a sucrose pipet transfer double normal weight of Steffen's waste or wash waters into a 100-cc. flask. Add two drops of phenolphthalein, and add slowly, under constant shaking, a concentrated solution of slightly acidulated lead acetate (about 450 grains lead acetate, and 2 cc. acetic acid per liter) until the red color disappears. Then add about 2 cc. more or sufficient to break up the milky precipitate, fill up to mark, filter, and polarize.

SACCHARATE CAKE AND SOLUTION FROM COOLER—These materials contain too much caustic lime to be completely decomposed by acetate of lead, but by ending the reaction with this solution the danger of an excess of acetic acid is avoided, and no further clarification is required. The method adopted is as follows:

> To normal weight of the material add dilute acetic acid until the red color imparted by two drops phenolphthalein disappears for the first time. The red color soon returns upon further shaking, and then complete the decomposition by an excess of concentrated neutral lead acetate. (About 450 parts of lead acetate to 1 liter of water, plus 1 cc. concentrated acetic acid.)

DETERMINATION OF SUCROSE AND RAFFINOSE IN MOLASSES

The old Herzfeld method works well with ordinary sugarhouse products, but when Steffen house molasses has to be analyzed the results are often far from satisfactory. The reason therefore is not hard to find. This molasses contains such large amounts of the salts of lime, potash, and soda, mostly as carbonates, that a part of the hydrochloric acid is neutralized thereby and therefore the inversion is not completed in the time specified. To try to overcome this difficulty by an addition of more acid or longer heating is not advisable, as the composition of the molasses is not constant. Therefore, a considerable error would be introduced when such a modification was used on molasses with less salts, and often the chemist does not know what kind of molasses he is testing, nor is he able to estimate the amount of carbonates present.

Walker[3] describes an inversion process for the determination of sucrose by double polarization, which apparently showed a way out of the difficulties. His method for determination of sucrose in cane-sugar molasses is briefly as follows:

> Place 50 or 75 cc. of the solution used for direct polarization in a 100-cc. flask (in case 50 cc. are used add 25 cc. water) and heat in a water bath to 65° C. Remove from bath, add 10 cc. of a

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[1] Presented before the Division of Sugar Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Z. Zuckerind. Landw.*, 727 (1898).

[3] THIS JOURNAL, **9**, 490 (1917).

mixture of equal volumes of hydrochloric acid (sp. gr. 1.188) and water, allow to cool down spontaneously in air for 15 minutes, or as much longer as may be convenient, then cool in water to room temperature, make up to 100 cc., and polarize as usual. In the case of low-grade products which have been clarified with a large excess of basic lead acetate, it is imperative that the excess alkalinity be neutralized before heating, this being best accomplished by the addition of 1 cc. (or 2 cc. in exceptional cases where a large excess of dry lead acetate has been used) of the dilute acid used for inversion.

When this method was applied to Steffen house molasses, it was found that the inversion was not completed within the time mentioned, more acid, longer time, or both, evidently being required. After a considerable amount of experimental work the method was finally adopted with the following modifications:

(1) The hydrochloric acid used is prepared by adding 40 cc. of water to 60 cc. of concentrated acid, in place of 50: 50 in the original method.
(2) One cubic centimeter of this acid is always added before heating.
(3) The contents of the flask is heated to 70° C. on the water bath (in place of 65° C.).
(4) The time of inversion before cooling is increased to 45 minutes.
(5) The chloride of lead precipitated is removed by filtration before the zinc dust is added.

Thus, the procedure is carried out in this manner:

Weigh out double normal weight of the molasses and transfer to a 200-cc. flask with water. Add basic lead acetate until no more precipitate is formed (25 cc. will generally be about right), fill up to mark, mix well, filter, and polarize in a 100-mm. tube. The reading multiplied by 2 gives direct polarization. Pipet 50 cc. of the filtrate to a 100-cc. flask, add 25 cc. water and 1 cc. hydrochloric acid (40 cc. water to 60 cc. concentrated hydrochloric acid). Insert a thermometer in the flask, and heat the contents on a water bath to 70° C. Remove the flask from the water bath and introduce 10 cc. of the dilute hydrochloric acid. Let stand in the air at room temperature for at least 45 minutes, cool, fill up to mark, and filter. Add a knife point of zinc dust, filter the solution and polarize again.

DETERMINATION OF MOISTURE IN DRIED PULP

Although it is of great importance to keep the moisture of dried pulp as constant as possible within narrow limits, the control thereof by the laboratory has been very unsatisfactory on account of the long time required for drying, even when vacuum ovens are available. In some plants the drying time has been cut down to one hour, and the moisture calculated by means of a factor in order to obtain at least an approximate result rapidly. But even so, a large amount of pulp has time to pass through the drier before the results are known. Therefore, a method of shortening the time of the determination, and at the same time giving the moisture accurately, ought to be of great value for the control of the drier work. The moisture tester[4] is an apparatus for distilling off the water contained in the sample, and is especially, and hitherto probably exclusively, used for the determination of moisture in grain. The grain is immersed in oil and heated to a specified temperature (in most cases to 190° C.) at which all the water distils off, to be collected in a cylinder so graduated that the reading of the liquid gives the percentage of moisture in the sample. As 50 or 100 grams of material are taken, the moisture present can be determined within 0.1 to 0.05 per cent.

As no information was available as to the procedure to be followed for determination of moisture in pulp, it became necessary to ascertain experimentally the amount of material to be taken, the volume of oil, and the temperature. Time did not permit a thorough investigation of all details, but the results obtained with the following method checked very well with the percentage of moisture found after 12 hours of drying at 105° C. in an ordinary drying oven.

Weigh out 50 grams of the pulp and transfer to distilling flask. Add 250 cc. of oil, and heat until the thermometer registers 190° C.

The whole operation is finished in 20 minutes. The apparatus is inexpensive and the oil can be used over and over again. This apparatus ought to be found in every sugarhouse laboratory.

Some experiments were also made to find out if the apparatus could be used for the determination of water in other sugarhouse products. With pressed pulp no satisfactory results were obtained, as the large amount of water present (about 85 per cent) caused excessive foaming. This can, of course, be overcome by the use of small amounts of sample, but then the accuracy of the method will be greatly decreased.

Water in molasses, fillmass, and sugar can be found by this method. Use 50 grams of material, 150 cc. of oil, and heat slowly to 170° C. However, variations of the materials may make modifications in the amounts necessary, and so far not enough experimental work has been done to ascertain the influence thereof.

DETERMINATION OF GUMS IN DIFFUSION JUICE

Where the apparatus for determination of potash by means of the centrifugal method is available, it will probably be of interest to know that the same can also be used for the determination of gums in diffusion juice.

To 5 cc. of diffusion juice add 0.5 cc. concentrated hydrochloric acid, and 15 cc. of 95 per cent (volume) alcohol. Mix well and let stand in water of about 70° C. for 15 minutes. Mix, transfer to a potash flask, and spin in motor-driven centrifugal for 15 minutes. Each degree on stem corresponds to 0.04 per cent of gums.

The absolute percentages obtained in this manner may not always be correct, but the figures are of considerable comparative value, since they indicate irregularities in the battery work, decomposed beets, and in a general way aid in comparing the beets of one plant with those of another.

The test is always run in duplicate (this is necessary to balance the centrifugal) and the mean of the two readings is taken.

PREPARATION OF STANDARD ACID

Many years ago the "Vereinslaboratory" in Berlin worked out the use of borax as a standard of preparation of normal solutions. As this salt furnishes an excellent check for such solutions, it is surprising that it is never mentioned in the chemical handbooks. The reason may be that borax loses some of its crystal water quite rapidly, but as the recrystallization thereof is very simple and rapid, this does not prevent its use. In the hands of men with little analytical experience or scientific education, it is probably the most accurate check available.

Commercial borax is recrystallized twice, C. P. borax once, preferably by letting the hot, concentrated solution (100 grams to 100 cc.) drop through a filter paper in a dish placed in cold water, under constant stirring. It is absolutely necessary to have the crystals form rapidly, under constant stirring, as large crystals are liable to enclose particles of the mother liquor. The fine crystals are washed once or twice with cold water, and the excess of water is removed by suction. Part of the moisture remaining is eliminated by pressing the crystals between filter papers until the papers no longer show any indication of moisture. The crystals are left to dry in the air, at room temperature, for 24 to 72 hours, depending upon the moisture in the air of the room. In winter, if no steam vapor is present, 24 hours are generally sufficient. No heating or drying in desiccators is permitted, as then some of the crystal water is lost.

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[4] For complete description of the apparatus and directions for its use see *U. S. Dept. Agr., Bur. Plant Industry, Circ.* **72**.

The high molecular weight of this salt will practically eliminate the effect of errors due to slight inaccuracy in weighing, or small impurities still present. Five grams of borax correspond to 26.2 cc. of normal acid; 19,109 grams to 1/10 normal, and 6.825 grams to 1/28 normal acid.

Methyl orange is generally recommended as an indicator for borax solution, but it is somewhat lacking in sharpness, especially in dilute solution. This difficulty has now been overcome by the use of dimethylamidoazobenzene. This indicator is prepared by dissolving 1 gram of the salt in 1 liter of alcohol. The end point is very sharp.

High-Speed Stirring as an Aid to Chemical Action[1]

By C. H. Milligan and E. Emmet Reid

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The relation of speed of stirring to velocity of reaction has been studied in the ethylation of benzene and in the hydrogenation of cottonseed oil in presence of nickel. In both cases the reaction rates are nearly proportional to speed of stirring.

CONTACT is conceded to be essential to chemical action, and it is usual to shake or stir mixtures to facilitate reactions, but quantitative data connecting the violence of the agitation with the rates of reactions are lacking. Such data are desirable for the design of equipment. Of course, conclusions drawn from small-scale laboratory experiments are not to be applied recklessly to plant apparatus.

Where we have two consecutive reactions, one of which is extremely rapid and the other slow, the over-all velocity depends on the slow reaction and is related to the circumstances that favor or hinder it. If we consider the mutual solution of the reactants as the first of the two reactions followed by a chemical change, we come to the conclusion that if the desired reaction is rapid but the rate of solution is slow, the reaction rate will be related to the rate of stirring, while if the solubility is great and the reaction comparatively slow, stirring will be of little importance. The present investigation is a preliminary study of the relation between speed of stirring and reaction rate in several non-homogeneous systems.

In the action of sulfur dioxide on benzene in the presence of aluminium chloride, stirring has little influence, since the gas dissolves readily anyway and the reaction rate is probably slow, but the absorption of ethylene by benzene in presence of aluminium chloride and the hydrogenation of cottonseed oil using nickel as catalyst are enormously accelerated by intensive stirring.

With the apparatus used by the authors and over the range covered by their experiments, the rates of these two reactions are roughly linear functions of the speed of stirring, and may be approximately expressed by $v = a + br$, in which v is rate of gas absorption and r is speed of stirring. The rate when the gas is only bubbled through is a, and b is a constant for a particular stirrer.

In the ethylation of benzene, a has a considerable positive value since the gas is moderately soluble in the liquid, while in the hydrogenation experiments a is negligible. Here the absorption of hydrogen increases faster than the rate of stirring for low speeds, the relation becoming linear at higher speeds. In Fig. 1 the absorptions in cubic centimeters per minute are plotted against speeds of stirring in thousands of revolutions per minute.

At 13,000 r. p. m. 1 volume of benzene was reacting with 6.5 volumes of ethylene, and 1 volume of cottonseed oil in presence of 0.12 per cent nickel was taking up 2.3 volumes of hydrogen, whereby its iodine number was being lowered 2.6 per minute.

For the literature relative to the ethylation of benzene by ethylene and for details as to the products obtained, reference may be made to a previous article.[2]

Rapid stirring appears to aid the chlorination of toluene and of acetic acid, but quantitative comparisons have not been made.

THE STIRRER (FIG. 2)

The speed of the motor was 1700 r. p. m., which was multiplied about eight times by an arrangement of pulleys carried on a steel frame. Ball bearings were provided for the stirrer shaft and for the upper end of the countershaft. The speed of the motor was controlled by a variable resistance. The speed of the stirrer was measured by a speed counter, the end of which carried a toothed wheel which meshed with a thread

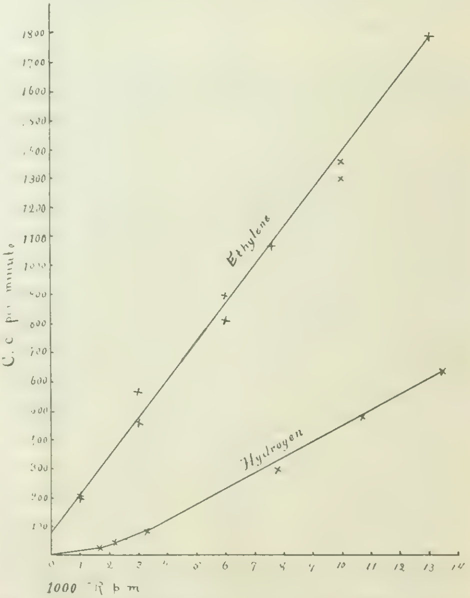

FIG. 1—VARIATION OF ABSORPTION OF HYDROGEN AND ETHYLENE WITH SPEED OF STIRRING

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[1] Received May 10, 1923.

[2] *J. Am. Chem. Soc.*, **44**, 206 (1922).

cut in the top end of the stirrer shaft. The speed counter was mounted on a swivel joint so that it could be snapped in and out of gear in taking the readings.

The reaction vessel was a glass bottle which was heated in a water or oil bath. The stirrer head was a disk, 37 mm. in diameter, carrying a bell-shaped projection at the bottom. Into the central cavity were drilled eight 2-mm. radial holes. The delivery tube for the gas terminated just beneath the bell. The stirrer shaft was surrounded by a tube which was carried by the frame above and passed tightly through the stopper, thus making a liquid seal for the stirrer shaft. To prevent swirling of the liquid large baffles were provided. These were carried by round rods passing through the stopper. By means of pliers applied to the projecting squared upper ends of these rods the baffles could be turned in so as to pass through the neck of the bottle.

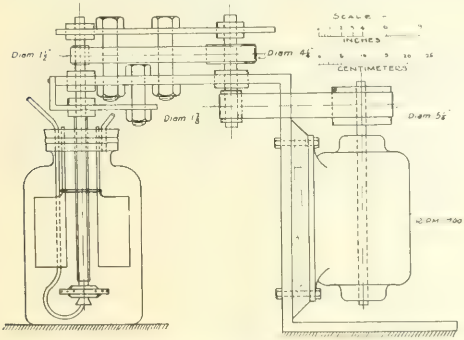

FIG. 2—THE STIRRER

EXPERIMENTAL

ETHYLATION OF BENZENE—A mixture of 250 grams of benzene and 50 grams of anhydrous aluminium chloride was kept at 80° C. and ethylene passed in, the speed of the stirrer being adjusted so that only an occasional bubble of gas escaped absorption. The rates of stirring and of gas flow were read and then the gas rate was changed. In a run in which constant conditions of stirring, etc., are maintained, the reaction velocity increases for a time and then remains fairly constant for a considerable period, changing gradually as the ethylation proceeds. The measurements made here were all from a single run. Sufficient time was allowed for the reaction to get well under way before starting readings and then the adjustments were made as quickly as possible and the readings taken with the passage of a minimum amount of gas so as to avoid great changes in the composition of the mixture. To produce monoethylbenzene 77 liters of ethylene would have been required, which is several times the volume necessary for the readings. The ethylene was passed through a meter and the time given is for 0.01 cubic foot or 283 cc. The results are given in Table I, the last column of which shows the roughly constant values of *b*.

TABLE I—ABSORPTION OF ETHYLENE

R. p. M.	Seconds per 283 Cc.	Cc. per Minute	Increase Due to Stirring	*b*
0	..	80	...	...
1000	84	202	122	122
1000	87	196	116	116
3000	30	565	485	162
3000	37	457	377	126
6000	19	896	816	136
6000	21	810	730	122
7600	16	1065	985	129
8000	15	1135	1055	132
10,000	12.5	1360	1260	126
10,000	13	1300	1220	122
13,000	9.5	1790	1720	132

HYDROGENATION—As the rate of hydrogenation varies with the proportion absorbed, the aim was to adjust gas flow and speed of stirring so that approximately 80 per cent of the hydrogen would be used up. The entering and emerging gas streams passed through two flowmeters placed side by side. The capillaries for these were cut from the same piece of tubing, the one on the exit side being just five times as long as the other, so that when the two read the same the absorption was just 80 per cent. The flowmeters were calibrated separately. The results are not so satisfactory as those on ethylation on account of the greater number of variables, but they show the same trend. Two runs were made with different preparations of catalyst, both nickel suspended on infusorial earth. The data from the first run are plotted in Fig. 1 and the results of both are given in Tables II and III. As in the ethylation experiments, the readings were made within a short period of time so as to mimimize the effect of changes due to progressive hydrogenation.

The three determinations in which the hydrogen was entirely absorbed are marked by (*). In these the amounts taken up are much smaller than in corresponding experiments with excess of hydrogen.

TABLE II HYDROGENATION
(Oil, 250 grams; catalyst, 1.5 grams; 20 per cent nickel)

R. p. M.	Hydrogen, Cc. In	Absorbed	Per cent	Cc. per 1000 R. p. M.
	At 180° C.			
1670	50	25	50	15
2200	50	41	82	19
3300	95	81	86	25
7800	350	298	85	38
10,700	565	475	84	44
13,500	755	633	84	47
13,500	433	433	100	32*
	At 185° C.			
5900	433	361	83	61
6800	488	407	83	60
7600	515	425	83	56
7500	242	242	100	32*

TABLE III -HYDROGENATION
(Oil, 250 grams; catalyst, 3 grams; 10 per cent nickel)

R. p. M.	Hydrogen, Cc In	Absorbed	Per cent	Cc. per 1000 R. p. M.
	At 180° C.			
1580	33.5	27	80	18
1800	56	42	75	23
2240	45	36	80	16
3400	158	126	80	36
7800	362	272	75	35
9000	362	272	75	30
10,200	473	355	75	34
12,850	517	413	80	32*
	At 190° C.			
4600	247	198	80	43
7200	427	360	84	50

The following experiments were made on the chlorination of toluene and acetic acid:

Into 400 grams of toluene at 100° C. chlorine was passed while stirring with a silver stirrer at 6000 r. p. m. There was practically total absorption at 1100 cc. per minute, the chief product being benzyl chloride. In the presence of a trace of ferric chloride the gas was absorbed as rapidly as it could be admitted.

Under the same conditions, 6000 r. p. m. and 100° C., 475 grams acetic acid, containing 17.5 grams of red phosphorus which had been rubbed to a paste with a part of the acid, absorbed chlorine as rapidly as it could be conveniently passed in, averaging about 1470 cc. per minute. During the second hour the rate averaged only 715 cc. per minute. At the end of about an hour all the phosphorus had dissolved.

A. P. Strietmann, president of The Biscuit and Cracker Manufacturers' Association, has founded a Research Fellowship at the University of Minnesota on fermentation problems arising in the industry of which he is the head. This research will be conducted in the Department of Biochemistry under the direction of C. H. Bailey. A. H. Johnson has been selected to carry on the work under this fellowship.

Influence of Starch on Strength of Wheat Flour[1]

By **J. H. Buchanan** and **G. G. Naudain**

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It has been shown that sizes of starch grains may be measured quickly and accurately by the method described. Tests on seven typical flour samples indicate a relationship between sizes of grains and strength of flours. Smaller starch grains tend to indicate a stronger flour.

Whether this relationship is due to actual colloidal properties of the starch or whether it simply reflects the condition under which the constituents were formed, is yet to be determined.

A POSSIBLE relationship between the starch of wheat flour and flour strength has been suggested by various investigations. Armstrong[2] indicated a variation in sizes of the starch grains of wheat flour. Jago,[3] by viscosity measurements, showed the smaller grains to give greater absorption. With the addition of 20 per cent of starch to flour he found the effect upon the absorption to depend upon the size of the starch grains. The flour, with added rice, showed the greatest absorption, wheat second, and potato the lowest. The sizes of the grains in millimeters were as follows: rice, 0.0050 to 0.0076; wheat, 0.002 to 0.052; potato, 0.06 to 0.10. Baking tests indicated a slight advantage in favor of the starches having the smaller starch grains. Hardy[4] makes this statement:

> The power of dough to retain its shape may be due, in some cases, primarily to the nature and number of starch grains. Whatever the influence of starch grains may be, they operate as passive agents; the active mechanical properties of dough, its tenacity and ductility, are due to the protein in complex gluten.

Snyder[5] believed starch to be without effect in influencing the baking strength. The more recent work of Rumsey[6] shows the value of diastatic enzymes in flour. Collatz,[7] in his study of the effect of addition of diastatic enzymes, arrived at the conclusion that the starch of strong flour was more easily hydrolyzed than that of weak flour.

It is evident that the literature does not give a very definite idea of the importance of starch with regard to strength of flour. Upson and Calvin,[8,9] Gortner and Doherty,[10] and Sharp and Gortner[11] have shown the necessity for a consideration of the colloidal properties of gluten. It was with the idea of determining what the colloidal properties of starch might indicate, with respect to flour, that this problem was undertaken.

EXPERIMENTAL

In this work seven typical flours, upon which baking tests had been run in order to determine loaf volume, were examined for the purpose of determining what influence the size of the starch grains might have. The range of the loaf volumes is given in Table III.

Measurements were made to determine the size of the starch grains in the flours examined. Use was made of a high-power microscope equipped with a micrometer eyepiece. This micrometer was standardized against a Thoma chamber so that each division of the scale corresponded to two microns.

With this equipment the sizes of the starch grains may be measured quickly and accurately.

It was found that the starch grains, when examined in this manner, could be grouped in two classes—those having diameters of 7 microns or less, and those having diameters of 8 microns or more. To show the accuracy of the measurements Table I is included. It will be noted that only those grains which would be classed as large are included.

TABLE I -DIAMETER OF LARGE STARCH GRAINS IN MICRONS

	Set 1	Set 2	Set 3
	18	14	12
	8	22	16
	24	16	8
	12	32	24
	24	24	20
	12	20	20
	19	22	12
	10	36	28
	24	22	14
	10	16	36
	16	16	26
	14	20	14
	10	14	12
	12	14	8
	22	22	26
	14	18	8
	16	22	12
	20	12	16
	14	18	14
	18	14	18
	16	13	18
	30	18	16
	22	12	10
	28	12	10
	16	8	26
	20	12	20
	22	12	16
	20	30	18
	14	12	20
	..	16	24
	..	22	22
TOTAL	505	561	544
AVERAGE	17.4	18.09	17.5

In Tables II and III are given the data obtained in the examination of the seven samples of flour. Table II indicates the percentages of starch grains of different sizes as found in the samples. Table III shows the loaf volume, percentage of small grains, and the average size of all the grains in each sample of flour. The sizes are diameters of the grains measured in microns.

TABLE II PER CENT OF STARCH GRAINS OF DIFFERENT SIZES IN SAMPLE

Diameter of Starch Grains in Microns	Sample Number						
	15	13	1	6	5	2	11
30	1.00	0.60	0.90	1.60	1.90	2.20	4.00
25 to 29	0.90	1.00	2 30	1.60	1.90	2.20	2.90
20 to 24	4.50	3.40	6.00	3.90	5.40	9.90	6.90
16 to 19	5.50	5.50	5.00	5.50	5.80	5.70	6.70
12 to 15	4.00	2.90	2 80	2.90	3.10	1.20	1.30
8 to 11	0 90	0.50	0.50	1.80	2.10	1.00	0.20
0 to 8	83.20	86.10	82.50	82.70	79.80	77.80	78.00

TABLE III—COMPARISON OF LOAF VOLUME WITH PER CENT OF SMALL GRAINS AND AVERAGE SIZE OF ALL GRAINS

Sample No.	Loaf Volume Cc.	Per cent Small Grains	Average Size of All Grains Microns
15	1710	83.20	6.69
13	1640	86.10	6.76
1	1540	82.50	7.16
5	1400	82.70	7.72
6	1415	79.80	6.90
2	1310	77.80	8.21
11	1265	78.00	9.31

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[1] Received April 16, 1923.

[2] Supplement form Board of Agriculture (England), **17**, 45 (1910).

[3] "Technology of Breadmaking," p 322.

[4] *Ibid.*, p. 319; Supplement form. Board of Agriculture (England), **17**, 52 (1910).

[5] *U S Dept Agr., Office of Expt Sta , Bull* **101**, 56

[6] American Institute of Baking, *Bull.* **8**.

[7] *Ibid.*, *Bull.* **9**.

[8] *J Am Chem Soc* , **37**, 1295 (1915)

[9] Nebr. Agr. Expt. Sta., *Research Bull.* **8**.

[10] *J. Agr. Research*, **13**, 389 (1918).

[11] *J. Phys. Chem.*, **24**, 101 (1920).

DISCUSSION

An examination of Tables II and III will show that there is a relationship between the sizes of the grains of starch and the strength of flour. With the exception of Sample 15, the flours fall in an order that would indicate that the greater the percentage of small grains the stronger the flour. Sample 13, with a loaf volume of 1640 cc., has 86 per cent small grains. Sample 1 shows a loaf volume of 1540 cc., and 82.50 per cent small grains. Sample 6 shows a volume of 1415 cc. and 79.8 per cent small grains. Sample 11, with a volume of 1265, shows 78.00 per cent small grains.

A consideration of loaf volume with the percentage of small grains is not sufficient. By comparing Sample 1 with 6, and 2 with 11, we find very little differences in the percentages of small grains. However, an explanation is offered when we take into consideration the average size of all the grains, and the percentages of grains of different sizes. Sample 1, with a greater loaf volume than Sample 6, shows only 0.6 per cent of grains that are 30 microns or greater in diameter, while Sample 6 has 1.6 per cent of grains of that size. Again, Sample 2 shows a greater loaf volume than Sample 11. If the average sizes of all starch grains are examined, it will be found that the average size of Sample 2 is 8.21 microns, while that of Sample 11 is 9.31 microns. Also, Sample 11 shows 4 per cent of the grains having diameters greater than 30 microns, while Sample 2 has 2.20 per cent. It is believed, then, that the size of the starch grains is a factor in determination of strength of flour, with the smaller grains indicating the stronger flour.

In view of conflicting opinions in the literature with regard to the action of various reagents on starch grains of different sizes, it is not so easy to give a reason for the foregoing conclusion. It may mean that smaller grains indicate a better colloidal condition. The colloidal properties of the gluten have been held by Gortner and Doherty[10] and others to be an important factor in the determination of strength of flour. It may be that the properties of the starch simply reflect the conditions under which the various constituents of the wheat berry were formed. Further work is now in progress to determine this point.

Quantitative Aspects of the Kreis Test[1]

By George E. Holm and George R. Greenbank

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The intensity of the Kreis test of samples of an oxidized fat is proportional to the amount of oxygen it has absorbed; or, the amounts of fat necessary for equivalent color intensities are inversely proportional to the volumes of oxygen absorbed.

The intensity of the Kreis test is not proportional to the rancidity or tallowiness of a fat. A rancid fat will give the Kreis test, but many fats that have absorbed large quantities of oxygen show only faint traces of rancidity, or none, yet give intense Kreis tests. Some evidence is found to indicate that oleic may be the only unsaturated acid in fats that gives the Kreis test when autoxidized.

Absorption of free oxygen is not necessary for the production of Kreis test by a fat. Exposure of a fat to light without the presence of free oxygen produces a change which causes a Kreis test.

OF ALL the methods that have been proposed for the detection of rancidity in fats, none has proved of greater value than the phloroglucinol-hydrochloric acid test first studied by Kreis.

Many objections to the use of this test have been raised. Winckel[2] objected to it because it is not specific for aldehydes and ketones found in rancid fats, because the depth of color produced is not proportional to the degree of rancidity, and because the test is too delicate. Kerr[3] ascribes the failure of its widespread application to (*a*) confusion of ideas as to exactly what is meant by rancidity, and (*b*) the fact that when a fat has become rancid its condition is so clearly evident that no chemical test is needed to recognize it. In his work he found that (*a*) all rancid fats give the Kreis test roughly but not in proportion to the rancidity, and (*b*) sweet fats do not give the Kreis test—except, in a few cases, cottonseed oil. He also agrees with Winckel that the test is too delicate and not specific.

Confusion with regard to the status of the Kreis test has been due to the fact that those factors concerned in the production of rancidity and those factors involved in producing the test are not well understood. Quantitative data are therefore lacking.

Rancidity has been ascribed to an oxidation process, and the observation that the presence of air favors the development of rancidity has been confirmed by numerous workers. Wagner, Walker, and Ostermann[4] claim, however, that rancidity can be produced by light in the absence of air.

That air, and especially oxygen, is a factor in the production of rancidity[5] of fats or tallowiness in butterfat has been shown in the work of the authors. Butterfat exposed to the action of oxygen will soon lose its color and give simultaneously a strong Kreis test, and will liberate iodine from potassium iodide in proportion to the amount of oxygen taken up. These and other tests upon the product substantiate the views of Winckel and of Vintelesco and Popesco that peroxides are formed. Oleic acid and triolein acted upon by oxygen give the same characteristic tallowy or rancid odor and the Kreis and iodine liberation tests. These experiments furnished only a qualitative basis for comparison of two fats. Fats were therefore studied quantitatively with reference to the amount of oxygen absorbed.

EXPERIMENTAL

A gastight stirrer was fitted into a flask containing a weighed amount of fresh, dry butterfat. This flask, containing an inlet and an outlet tube, was evacuated and filled with oxygen from a gas buret. The flask was kept at a constant temperature and the stirrer run at high speed, and the volume of oxygen absorbed was noted from time to time. The induction period varied with the freshness of the sample of fat. With fresh butterfat this period was approximately 3 hours, with lard approximately 1.5 hours, etc. Older samples showed shorter induction periods. Samples were withdrawn through the outlet tube at regular intervals and various tests were performed.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *Z. Nahr. Genussm.*, **9**, 90 (1905).

[3] THIS JOURNAL, **10**, 471 (1918).

[4] *Z. Nahr. Genussm.*, **25**, 704 (1913).

[5] The term rancidity as used throughout this paper excludes hydrolytic changes in the fats.

In order to determine the amounts of fat necessary to give Kreis tests of equal intensity, a small amount of each sample was weighed into a small flask and dissolved in a definite volume of ether. Trial tests were made with varying amounts of each sample until the amounts were ascertained which gave equivalent colors with the Kreis phloroglucinol reagent. Prior to the test the ether contained in each tube was evaporated by placing the tube in a water bath kept at 40° to 50° C., since it was found that the absence of ether gave more clear-cut results. The volumes of solution of the samples used for each test ranged from 3 cc., with fats but slightly oxidized, to 0.10 cc., or less in the case of highly oxidized fats. The amount of hydrochloric acid used in each case was 1 cc. As a rule the best results were obtained when the amount of fat used in each test ranged from 0.10 to 0.50 gram.

The iodine liberation test was carried out by ascertaining, in the usual way, the amount of iodine liberated from a slightly acidified potassium iodide solution by 1 gram of fat in 24 hours.

The results obtained upon pure butterfat are found in Table I.

TABLE I THE PROPERTIES OF A DRY BUTTERFAT (400 GRAMS) THAT HAS ABSORBED VARIOUS AMOUNTS OF OXYGEN AT 95° C.

Oxygen Absorbed Cc	Acidity N/14 HCl per 5 G. Cc.	Iodine No.	Iodine Liberated from KI in 24 Hours by 1 Gram of Fat G.	Kreis Test Amount Necessary for Equivalent Color Intensities G.	K. Amounts Fat × Vol. Oxygen	K Basis of 100 Grams Fat
0.00	0.52	31.50	....	Negative	.	...
5.00	0.88	31.44	.	0.20		
300	0.90	30.42	0.0006	0.014	4.20	1.05
500	1.05	30.80	0.0010	0.0090	4.50	1.25
800	1.65	29.18	0.0017	0.0055	4.40	1.10
1100	2.00	28.70	0.0026	0.00385	4.23	1.06

The results shown in this table indicate that in the autoxidation of butterfat there is an increase in the acidity and a decrease in the iodine number. The liberation of iodine from potassium iodide was found to be a slow reaction, but was found to be a comparative measure of oxidations when carried out under similar conditions.

The relation of acidity to oxidation will be discussed in another publication.

With regard to the tests mentioned, it is evident that neither the iodine number nor the iodine liberation test is sensitive enough to detect small changes through oxidation. The intensity of the Kreis test, however, was found to be very marked with small changes in oxidation. Furthermore, *the color intensity is directly proportional to the amount of oxygen absorbed by a fat; or, the amount of a fat necessary to give equivalent colors with the Kreis reagent is inversely proportional to the amount of oxygen absorbed, up to a certain limit.* The rigidity of this proportionality is shown by the figures obtained by the products of the oxygen absorbed and the amount necessary to give the chosen color intensity in each case. Where tests are carried out at various times and where a standard with a fat is difficult to maintain, a methyl red standard at pH 4.8 has been found very convenient for purposes of comparison. Knowing the direct relationship between oxygen absorbed and the Kreis test, it is possible to calculate that in the case of a butterfat that has absorbed 1 cc. of oxygen per gram of fat, 11 mg. are necessary to produce such a color intensity. In case of a fat having absorbed 1 cc. per 100 grams, 1.10 grams should give this intensity. The sensitiveness of the Kreis test and its strict quantitative relationship to the oxygen absorbed make it an exceedingly good measure of the oxygen absorbed, other changes being excluded.

Lard contains a high percentage of unsaturated fatty acids, not oleic. Treating a fresh sample of lard under conditions similar to those used in Experiment 1 on butterfat, it was again found, as shown in Table II, that the intensity of the Kreis test upon samples of oxidized lard was proportional to the amount of oxygen absorbed.

It is noted, however, that for equivalent amounts of oxygen absorbed by butterfat and lard per 100 grams of substance the amount of oxidized lard necessary to give a Kreis test of a certain intensity is greater than the amount of oxidized butterfat.

TABLE II RELATION OF INTENSITY OF KREIS TEST TO AMOUNT OF OXYGEN ABSORBED BY 450 GRAMS OF LARD AT 95° C.

Oxygen Absorbed Cc.	Kreis Test Weight of Fat Necessary for Equivalent Color Intensities G.	*K.* Cc. of Oxygen Absorbed × Weight for Equivalent Color	*K.* Basis of 100 Grams Fat
90	1.00	90.00	20.00
180	0.60	108.00	24.00
360	0.25	90.00	20.00
540	0.075	40.50	9.00

According to Lewkowitsch[6] approximately 49 per cent of the acids in lard is oleic acid, 10 per cent is linolic acid, and a small fraction is perhaps linoleic. Butter,[7] on the other hand, contains 36 per cent of its acids as oleic acid, and has no other unsaturated acids, as far as known. It will be shown later that the absorption of oxygen by oleic acid does produce compounds that give the Kreis test in a ratio approximately equal to that of butterfat. In view of this fact the foregoing table for lard would tend to show that the oxygen absorbed by lard in this case was taken up largely by the unsaturated linkages not oleic, and that this absorption does not give rise to compounds which produce a Kreis test. Unfortunately, no linolic or linoleic acid was on hand, so that it could not be definitely determined whether or not oxygen absorption by these acids produces compounds capable of giving a Kreis test.

It is extremely important to note here, however, that in no sample used was there more than the slightest trace of rancidity, even after an absorption of 180 cc. of oxygen in 450 grams of lard. If oxidized oleic acid is responsible for the rancid odor in oxidized butterfats, we must assume that in this case unsaturated acids other than oleic are largely involved.

The idea that there can be autoxidation without any noticeable rancidity was contrary to all general belief, and for this reason various other fats and oils were autoxidized and tested. No quantitative results were obtained upon these oils. Cottonseed oil, which gave practically no Kreis test, when autoxidized gave the Kreis test in increasing intensity but showed only a trace of a characteristic rancid odor. This may explain why sweet cottonseed oil will at times give a Kreis test. It is possible that oxygen may be absorbed without a proportional formation of compounds that give a rancid odor, but with a formation of those compounds that give the Kreis reaction.

Olive oil, which contains practically 93 per cent of its liquid acids as oleic acid, and 7 per cent as linolic, was next tried, with similar results.

These results indicate conclusively that for a fat the intensity of the Kreis test is proportional to the oxygen absorbed and is a measure of oxidation, but has no direct quantitative relation to the degree of rancidity as measured by the olfactory senses. That there is no direct quantitative relation may also be shown by absorbing in 110 grams of butterfat 10 cc. of oxygen and comparing this product with 100 grams of butterfat to which have been added 10 grams of butterfat which has absorbed 10 cc. of oxygen. The former will show tallowiness and a Kreis test, while the latter will give a Kreis test of the same intensity but will show little or no tallowy odor, which shows that as oxidation progresses tallowiness and the Kreis test are not developed proportionally. Preliminary tests have shown that mixtures of heptylic aldehyde and pelargonic acid added to fresh fat will produce a condition very similar to tallowiness of butterfat or rancidity of many fats. These compounds and other decomposition products of oxidized fats are undoubtedly the cause of the rancid odors, but neither of the two compounds mentioned above give the Kreis test. As oxidation progresses, therefore, it seems that the compounds giving the tallowy odors are not formed in stoichiometric ratio to the compounds that give the Kreis test. It is possible that as they are formed they are in some cases subsequently destroyed, or that various unsaturated compounds give different decomposition products.

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[6] "Chemical Technology and Analysis of Oils, Fats, and Waxes," II, 3rd ed., p. 780.

[7] *Ibid.*, II, 3rd ed., p. 833.

That the oleic acid radical is one constituent that may be concerned in the oxidation and formation of products which give the Kreis test, is shown in the following experiment, where oleic acid was autoxidized.

TABLE III—RELATION OF INTENSITY OF KREIS TEST TO AMOUNT OF OXYGEN ABSORBED BY 300 GRAMS OF OLEIC ACID AT 50° C

(Standard equivalent = pH 4.8 with methyl red)

Oxygen Absorbed Cc.	Kreis Test Amount Necessary for Equivalent Color Intensities G.	*K.* Weight of Fat Used × Amount of Oxygen Absorbed	*K.* On Basis of 100 Grams of Oleic Acid
60	0.076	4.56	1.52
90	0.050	4.50	1.50
130	0.038	4.94	1.63
175	0.027	4.72	1.57
475	0.010	4.75	1.58

As in the case of the fats and oils tried, the intensity of the Kreis test is proportional to the oxygen absorbed. Under the conditions under which the experiment was carried out there is no direct ratio between the intensity of the tests with butterfat and lard as compared with their oleic acid content when the unit of oxygen absorbed is the same per gram weight of fat. Two samples of the same fat autoxidized may or may not give equivalent weights for the same intensity of Kreis test when equivalent amounts of oxygen have been absorbed. It has been noted, however, that traces of water present affect the course of the reaction, and it is probable that if all fats tried were absolutely dry when autoxidized a definite ratio would be obtained between the Kreis tests and some one constitutional property of the fats.

Kerr[8] states that rancidity "can be absolutely prevented by the exclusion of oxygen." The contention has been made, by a few workers, however, that oxygen is not necessary for the production of rancidity, and this agrees with some further observations that the writers have made. Certain fats when sealed in a vacuum and exposed to sunlight will become rancid and will give a Kreis test. Some fats after prolonged storage without access of light have shown similar properties. It is improbable that the reaction which occurs *in vacuo* is identical with that which takes place when pure oxygen is absorbed. Properties of the color formed with the Kreis reagent indicate this.

Since the change that occurs in a fat that is stored *in vacuo* without access of light is very slow, and since few fats are subjected to the action of light at any time in their handling, it is doubtful if any slight action from this cause will have any bearing upon the Kreis test as previously discussed.

Detailed experimental work upon the nature of the reaction in fats stored *in vacuo* in sunlight will be the subject of another publication.

DISCUSSION

The experiments upon the oxidation of butterfat and lard reported here were carried out at 95° C., and consequently the question might be raised whether the reactions at this temperature would be comparable with reactions occurring at lower temperatures. Because of the time required for these autoxidation reactions at lower temperatures, it is not feasible to use these temperatures. Experiments carried out at 50° C. furnished results that were in good agreement with those reported. Results upon oleic acid at 95° C. agree well with those reported for 50° C.

The constants obtained for butterfat, lard, and oleic acid are of no great comparative value as they stand. They serve to indicate, however, that oleic acid will give the Kreis test in proportion to the amount of oxygen that it has absorbed. The results upon lard would indicate that some acid radical or radicals present in this substance will not give the Kreis test when it absorbs oxygen. Assuming that the Kreis test that is produced when lard is oxidized is due to oxidation of the oleic acid radical, we might conclude that oxidation of linolic or linoleic acid radicals produces no compounds that are capable of giving the Kreis test. While the evidence points strongly that way, it can be determined with certainty only when these compounds are subjected to oxidation and the products are tested.

It is significant to note, however, that in all experiments which have been carried out, no case has been noted where there has been appreciable oxidation without giving a Kreis test. This would indicate that, whatever the acid radicals, in addition to oleic, that give rise to the Kreis test, they oxidize simultaneously with other unsaturated radicals that do not give the test. The fundamental nature of the reactions is evidently the same and the autocatalyst for one is also a catalyst for the others.

This observation makes it quite certain that the Kreis test is always a good measure of the degree of oxidation where at least one radical is present which is capable of producing it under such conditions. This is especially true with butterfat, since the oleic acid radical is probably the only unsaturated radical present. In the case of this fat the test has been used with success to follow oxidation changes during storage.

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[8] *Cotton Oil Press*, **5**, 45 (1921).

Carbon Tetrachloride Fire Extinguishers

According to tests made at the Pittsburgh Experiment Station of the Bureau of Mines relative to the hazards to fire-fighters from gases and smoke resulting from the application of carbon tetrachloride extinguisher to electric arcs, burning insulation, or fires such as may occur in electrical apparatus and machinery, it was found that the application of 1 cubic foot of fire extinguisher to electric arcs and burning insulation in a chamber of 1000 cubic feet capacity developed phosgene, chlorine, and hydrogen chloride in quite dangerous concentrations. Carbon tetrachloride vapors, sulfur dioxide, and carbon monoxide were also formed in less dangerous concentrations.

These tests confirm conclusions drawn from previous tests by the Bureau of Mines that it is dangerous to breathe the gases that may be generated from a 1-quart carbon tetrachloride extinguisher applied to a fire in a confined space from which escape is difficult or impossible, and from which the gases would not be removed by ventilation.

So far as is known, carbon tetrachloride extinguishers are the most effective and satisfactory of any that can be applied to electrical fires with safety from shock to the operator. Arcs of 60 amperes direct current and 220 volts and 35 amperes and 500 volts were easily extinguished with a 1-quart carbon tetrachloride fire extinguisher.

Formation of Formic Acid by Caramelization of Cane Sugar[1]

By Stephen G. Simpson

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The numerical results given in this article indicate that (1) formic acid is produced in considerable quantities by the caramelization of sugar; (2) the amount of formic acid produced is governed by the extent of the caramelization, which in turn is determined by the temperature and time of heating; (3) food products which have not been heated above 160° C. should have produced no appreciable amounts of formic acid by caramelization of sugar; (4) knowing the conditions of temperature and time of heating in the preparation of a food product of known sugar content, the amount of formic acid which should be present due to caramelization can be approximately estimated.

Work is being continued with respect to starches and other carbohydrates occurring in food products.

THE detection and determination of formic acid has in the last few years played an increasingly important part in the analysis of food products. The fact that small amounts of the acid inhibit bacterial growth makes it an efficient preservative, and cases have been cited[2] where it has been so used in commercial products. It has been shown that formic acid is also a natural constituent of some foodstuffs. Seeker,[2] for example, finds in jams, sirups, and other similar foods amounts of formic acid ranging from 0.0009 to 0.0130 per cent, and in dark beers and ales containing considerable caramel[3] amounts from 0.0010 to 0.0040 per cent. Whether or not formic acid is a natural constituent of honey, has been the subject of controversy, although Fincke,[4] Farnsteiner,[5] and Heiduschka and Kaufmann[6] have shown that the amount present is in any case less than 0.02 per cent. Kingzett and Woodcock[7] have shown that formic acid is produced by the slow oxidation of some terpenes, which would lead to the possibility of traces being found in products flavored with essential oils, and this has been verified experimentally by Seeker. Apparently, food products which in their preparation have been heated sufficiently to caramelize the carbohydrates they contain, show comparatively high percentages of formic acid. Thus, Seeker[2] finds in coffee extracts amounts of formic acid from 0.060 to 0.111 per cent calculated on the original coffee, and in samples of caramel amounts up to 0.602 per cent. Similar high values were obtained by the writer, and the values listed below show the effect of caramelization on the formic acid content of a few common commercial products.

	Formic Acid Per cent
Coffee, unroasted	0.000
Coffee, roasted	0.221
Cane sugar	0.000
Starch	0.000
Invert sugar sirup	0.026
Caramel	0.404
Oatmeal, charred	0.057
Wheat bran, charred	0.062

Since formic acid may be added to a food product as a preservative, and since in other food products it occurs naturally through caramelization of the sugars contained therein, it becomes of considerable importance to determine the exact conditions of temperature and time of heating which will

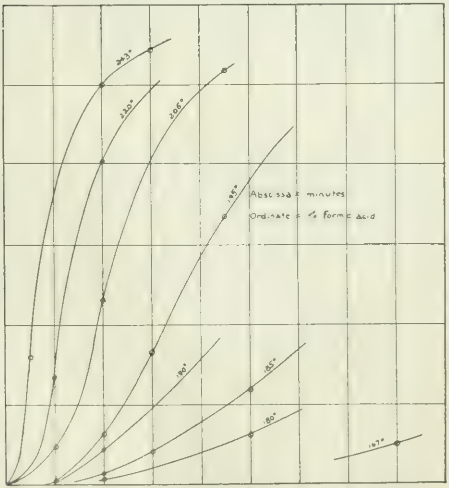

Fig. 1—Production of Formic Acid from Cane Sugar by Heating at Definite Temperatures for Varying Intervals of Time

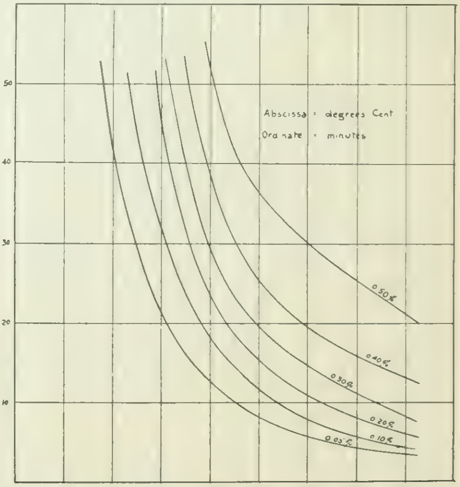

Fig. 2—Conditions of Temperature and Time Required for the Production of Definite Percentages of Formic Acid (Interpolated from Fig. 1)

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[1] Received May 16, 1923.

[2] Seeker, *J. Assoc. Official Agr. Chem.*, **1**, 210 (1915).

[3] *Ibid.*, **1**, 556 (1916).

[4] *Z. Nahr. Genussm.*, **23**. 255 (1912).

[5] *Ibid.*, **15**, 598 (1908).

[6] *Ibid.*, **21**, 375 (1911).

[7] *Chem. News*, **105**, 26 (1912); *J. Soc. Chem. Ind.*, **29**, 791 (1910).

cause the natural formation of formic acid, and to determine the amounts thus formed under these varying conditions. Knowing the conditions of time and temperature under which a food is prepared, it should be possible in many cases to make use of such data to determine whether or not any formic acid which may be found in the product has been added as such, or has been formed by natural changes.

EXPERIMENTAL

Samples of cane sugar, 10.0 grams in each case, were heated in loosely stoppered tubes in an oil bath under varying temperatures and for varying lengths of time. The samples thus prepared were analyzed for formic acid by the Fincke method,[8] which, in brief, consists in steam-distilling 100-cc. solutions of the samples to which 2 grams of tartaric acid have been added. The volume of the sample solution is kept constant by auxiliary heating, and in no case is the volume allowed to decrease appreciably. The vapors are passed through a suspension of calcium carbonate in water and thence through a condenser so that the volume distilled can be determined. After 1500 cc. have been condensed, the calcium carbonate suspension is filtered, the filtrate faintly acidified with hydrochloric acid and boiled 2 hours under a return condenser with 5 to 25 cc. of a solution containing 10 per cent mercuric chloride, 10 per cent sodium chloride, and 15 per cent sodium acetate. The precipitated mercurous chloride is filtered on a Gooch crucible, washed, dried, and weighed. The conversion factor is 0.0975. The results are corrected for a "blank" on the reagents by carrying them through a distillation under conditions identical with the analysis itself.

The values obtained for the caramelized samples of cane sugar are listed in the table, and are also expressed graphically in Figs. 1 and 2.

Temperature ° C.	Time of Heating Min.	Appearance of Sugar after Heating[a]	Formic Acid Mg.	Formic Acid %
145	20	*B*	0.0	0.000
	120	*B-C*	0.6	0.006
167	20	*B*	0.0	0.000
	35	*B-C*	0.0	0.000
	80	*F-G*	4.9	0.049
180	20	*E-F*	0.8	0.008
	50	*G*	6.1	0.061
185	10	*B*	0.0	0.000
	20	*F*	1.3	0.013
	30	*G*	4.0	0.040
	50	*H*	11.9	0.119
190	10	*B*	0.1	0.001
	20	*F-G*	4.3	0.043
195	10	*E*	0.4	0.004
	20	*G*	6.3	0.063
	30	*H*	16.6	0.166
	45	*H*	33.7	0.337
205	5	*C*	0.0	0.000
	10	*F*	4.8	0.048
	15	*G*	6.1	0.061
	20	*G-H*	23.1	0.231
	45	*H*	51.8	0.518
220	10	*H*	13.5	0.135
	20	*H*	40.1	0.401
243	5	*G-H*	16.0	0.160
	20	*H*	50.0	0.500
	30	*H*	54.8	0.548

[a] *A* = Sugar unchanged
B = Slightly yellow but granular
C = Superficially melted
D = Entirely melted, light yellow
E = Entirely melted, deep yellow
F = Entirely melted, light brown
G = Entirely melted, dark brown
H = Entirely melted, black

[8] *Z. Nahr. Genussm.*, **21**, 1 (1911); **22**, 88 (1912); **23**, 255 (1912); **25**, 386 (1915); *Biochem. Z.*, **51**, 253 (1913).

Chemistry of Wood[1]

VI—The Results of Analysis of Heartwood and Sapwood of Some American Woods

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THIS report contains the results obtained in the analysis of heartwood and sapwood of ten American woods. The work was undertaken to determine whether there is any uniform difference in chemical composition between sapwood and heartwood in either softwoods or hardwoods.

The methods of analysis used are the same as given in the preceding paper in this series.[2] All determinations were made in duplicate and the average is given in Table I.

DISCUSSION OF RESULTS

ASH CONTENT—There is no general agreement in the relative ash content of sapwood and heartwood in the species examined.

EXTRACTIVE CONTENT—In general, the extracts of ether, cold water, hot water, and 1 per cent sodium hydroxide are lower in the sapwood than in the heartwood of the softwoods. In the hardwoods the extractives are lower in the sapwood than in the heartwood of yellow birch, white oak, and yellow poplar, but the reverse is true of white ash and pignut hickory. Thus, from the standpoint of extractive content in sapwood and heartwood, the hardwoods analyzed are divided into two classes—one class following the order of the softwood, the other following the reverse course.

ACETIC ACID—The acetic acid obtained by hydrolysis is higher in the sapwood than in the heartwood of both classes of woods.

METHOXYL CONTENT—The relative percentages of methoxyl in the sapwood and heartwood of the species analyzed cannot be arranged in any general order.

PENTOSAN CONTENT—There is a tendency toward higher yields of pentosans in the sapwood than in the heartwood of the species examined. The difference in yields, however, is slight.

METHYL PENTOSAN CONTENT—The methyl pentosan content in sapwood and heartwood of the same class is quite uniform.

CELLULOSE CONTENT—For the relative cellulose content of sapwood and heartwood, the species analyzed, with the exception of yellow poplar, are grouped in a manner similar to that for extractives. All the softwoods examined have higher cellulose yields in the sapwood than in the heartwood. This tends to counterbalance the low extractives in the sapwood. One hardwood group, yellow birch and white oak with high extractives in the heartwood, has high cellulose content in the sapwood. The other group of hardwoods, white ash and pignut hickory with high extractives in the sapwood, has high cellulose content in the heartwood. The results obtained from the two yellow poplar samples, which are an exception to the foregoing scheme of grouping, can be explained by referring to the condition of the samples.

[1] Presented before the Division of Cellulose Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] THIS JOURNAL, **14**, 1050 (1922).

TABLE I—ANALYSES OF SAPWOOD AND HEARTWOOD OF SOME AMERICAN WOODS
(Results in percentage of oven-dry (105° C.) samples)

				Solubility in										In Cellulose				
Species	Sample	Moisture	Ash	Cold Water	Hot Water	Ether	1% NaOH	Acetic Acid	Methoxyl	Pentosan	Methyl Pentosan	Cellulose	Lignin	Pentosan	Methyl Pentosan	Alpha	Beta	Gamma
White ash:																		
No. 2 sapwood	179	5.34	0.61	5.81	6.41	1.17	21.77	3.23	4.70	19.85	2.40	50 38	26 95	18.83	1.60	74.67	13.67	11.66
No. 2 heartwood	180	5.45	0.30	2.24	3.40	0.43	19.59	2.31	5.36	19.90	2.25	53.56	27.39	16.75	1.34	64.68	24.58	10.84
No. 3 sapwood	181	4.91	0.57	5.25	7.02	0.88	21.93	3.70	5.66	20.16	2.63	49.72	27.39	19.67	1.60	55.11	28.29	16.50
No. 3 heartwood	182	7.42	0.32	2.12	4.46	0.46	18.97	2.66	5.20	19.87	2.46	53.40	28.38	17.34	1.47	42.45	33.22	24.33
Yellow poplar:																		
No. 1 sapwood	187	4.30	0.48	1.29	1.98	0.27	16 74	3.12	5.81	18.37	3.28	58.13	23.08	15.52	2.21	50.13	30.74	19.13
No. 1 heartwood	188	3.79	0.39	1.50	2.08	0.43	17.70	2.89	5.86	18.47	3.11	59.57	22.19	14.97	2.40	61.30	20.20	18.50
No. 2 sapwood	189	3.79	0.36	1.45	2.51	0.13	16.91	3.33	5.89	18.82	1 22	58.02	23.86	19.01	0.78	34.32	48.52	17.16
No. 2 heartwood	190	3.88	0.33	1.45	2.89	0.58	17.57	2.73	6.03	19.08	1.13	59.47	23.69	17.83	1.47	36.67	42.75	20.58
Pignut hickory:																		
No. 1 sapwood	191	3.54	0.40	4.91	6.45	0.29	19.11	3.58	5.56	18.18	1.11	56.08	21.87	16.90	1.30	51.55	21.92	26.53
No. 2 heartwood	192	3.90	0.45	2.07	2.95	0.36	15.10	3.08	5.79	18.64	1.02	58.81	22.85	16.20	1.39	59.44	23.74	16.82
Yellow birch:																		
No. 1 sapwood	207	4.92	0 26	1.05	1.98	0.48	16.77	2.34	5.66	21.36	1.66	58.91	24.69	20.72	1.13	52.15	32.90	14.45
No. 1 heartwood	208	4.76	0.40	4.16	5.69	0.81	20.51	1.78	5.46	20.37	1.39	56.88	24.62	21.87	1.12	61.17	23.23	15.60
No. 2 sapwood	213	4.28	0.18	1.74	2.10	0.88	19.78	3.75	5.47	22.30	1.82	56.57	27.76	22.19	1.71	52.40	26.82	20.78
No. 2 heartwood	214	4.36	0.23	2.76	3.96	0.99	21.14	2.83	5.27	23.21	1.07	54.93	28.13	21.81	1.04	53.56	25.00	21.44
White oak:																		
No. 1 sapwood	209	7.71	0.57	2.55	4.11	0.46	21.11	3.44	5.95	23.25	0.90	49.53	32.34	24.74	0.88	68.07	15.27	16.66
No. 1 heartwood	210	7.70	0.43	7.33	10.15	0.71	25.81	2.59	6.18	21.82	1.57	48.68	32.74	24.22	0.58	67.33	11.84	20.83
No. 2 sapwood	211	7.09	0.37	4.27	5.73	0.65	21.69	2.47	6.02	21.72	0 94	53.18	31.14	24.81	1.20	53.81	22.63	23.56
No. 2 heartwood	212	6.99	0.42	4.76	6.60	0.62	22.67	2.97	5.64	22.08	0.91	52.12	31.30	24.54	0.96	52.96	20.41	26.63
Bald cypress:																		
No. 1 sapwood	183	4.72	0.48	0.72	1.42	0.23	8.55	0.77	4.35	8.03	4.38	54.86	35.01	6.25	1.85	76.09	5.93	17.98
No. 1 heartwood	184	5.30	0.30	2.79	2.99	4.87	10.59	0.48	3.94	6 67	4.49	53.10	33.06	5.84	1.80	76.83	3.94	19.23
No. 2 sapwood	185	6.72	0.86	1.76	2.30	2.80	10.63	0.65	4.99	9 23	3 34	50.94	35.31	5.89	1.65	58.18	26.91	14.91
No. 2 heartwood	186	4.72	0.95	3.27	3.49	7.93	13.56	0.29	4.07	7 88	3.36	49.18	32.27	6.33	1.25	57.38	24.75	17.87
White pine:																		
No. 1 sapwood	193	3.90	0.23	3.55	5.15	5.46	17.16	1.68	4.16	9.31	2.14	54.25	26.51	6.81	2.09	54.56	17.47	27.97
No. 1 heartwood	194	2.92	0.42	5.97	7.68	3.62	19.15	1.43	4.60	8.56	1.00	50.23	26.14	7.12	2.02	57.29	22.42	19.29
Yellow cedar:																		
No. 1 sapwood	195	3.97	0.28	2.13	3.41	1.00	11.72	2.05	4.40	8.47	1.75	58.12	29.03	7.60	2.44	54.61	26.59	18.80
No. 1 heartwood	196	4.00	0.18	2.88	4.12	1.32	12.77	1.53	4.81	8.69	1.85	56.08	28.73	7.78	2.73	...	20.17	...
White cedar:																		
No. 2 sapwood	197	5.59	0.64	2.18	2.82	..	11.02	1.17	5.07	11.61	0.94	55.77	29.85	10.35	1.77	73.78	0.99	25.23
No. 2 heartwood	198	6.39	0.21	1.94	3.22	..	11 41	0.84	5 00	10.79	1.72	55.19	31.39	8.52	1.58	61.47	22.23	16.30
No. 3 sapwood	199	6.02	0.48	3.02	3 96	1.44	12.71	1.11	5.23	10.82	1.16	55.02	32.14	8.95	1.28	69.17	14.04	16.79
No. 3 heartwood	200	6.48	0.27	2.80	4.01	1.87	14.14	0.74	5.09	10.36	1.56	54.42	32.42	7.97	1.32	55.22	24.74	20.04
Incense cedar:																		
No. 1 sapwood	205	6.46	0.47	1.92	2.97	0.67	11.16	1.33	5.95	12.08	0.45	49.09	34.73	10.14	1.24	50.69	12.98	36.33
No. 1 heartwood	206	7.27	0.30	4.74	7.08	4.78	19 99	0.68	6.21	12.04	0.56	44.53	33.67	11.68	1.31	66.62	11.05	22.33

Both yellow poplar samples showed slight signs of decay in the sapwood. This condition would tend to increase extractives in the sapwood. The results show slightly higher extractives in the heartwood than in the sapwood, which indicates that on the basis of extractives yellow poplar is strictly a member of the first group of hardwoods. If it belongs to the first group, the cellulose content should be higher in the sapwood than in the heartwood, which is not the case. This can also be explained on the basis of the decayed condition which decreases the cellulose content in the sapwood, the reverse of what would be expected in sound yellow poplar.

LIGNIN CONTENT—In softwoods, with the exception of white cedar, the lignin content is higher in the sapwood than in the heartwood. In the hardwoods all species except yellow poplar have a higher lignin content in the heartwood than in the sapwood.

A study of the ratio between methoxyl and lignin is shown in Table II. A study of the results reveals the fact that the methoxyl-lignin ratio is approximately 50 per cent higher in hardwoods than in softwoods. This ratio averages less than 13 per cent in bald cypress. In Paper V of this series[2] it was shown that the methoxyl content of isolated redwood and live oak lignins was approximately 17.5 per cent. Bald cypress lignin could not meet these specifications and, consequently, it must differ in chemical composition from redwood and live-oak lignins.

PENTOSAN CONTENT OF CELLULOSE—The pentosan content has a slight tendency to run higher in the sapwood cellulose than in the heartwood cellulose, similar to the results obtained in the original wood.

METHYL PENTOSAN CONTENT OF CELLULOSE—In general, the methyl pentosan content is slightly higher in the heartwood cellulose than in the sapwood cellulose. A similar relation was found in the heartwood and sapwood of the original samples.

α-, β-, AND γ-CELLULOSE CONTENT OF CELLULOSE—The percentages of the three kinds of cellulose in sapwood and heartwood cellulose cannot be grouped in any definite arrangement.

CONCLUSIONS

From a study of the data given in this report the following conclusions may be drawn:

1—In softwoods the water, ether, and alkali extracts are higher in the heartwood than in the sapwood, and as a result the cellulose and lignin are correspondingly lower in the heartwood (except lignin in white cedar).

2—On the basis of extractives hardwoods are divided into two groups: (*a*) those with high extractives in the heartwood, and (*b*) those with high extractives in the sapwood. The former have high cellulose content in the sapwood; the latter in the heartwood.

3—Acetic acid by hydrolysis is higher in the sapwood than in the heartwood of both softwoods and hardwoods.

TABLE II—RATIO OF METHOXYL TO LIGNIN ON OVEN-DRY (105° C.) WEIGHT OF THE WOOD

		Lignin		CH_3O		$\frac{CH_3O \times 100}{\text{Lignin}}$	
Species	No.	Sapwood	Heartwood	Sapwood	Heartwood	Sapwood	Heartwood
White ash	2	26.95	27.39	4.70	5.36	17.4	19.5
	3	27.39	28.38	5.66	5.20	20.0	18.3
Yellow poplar	1	23.08	22.19	5.81	5.86	25.2	26.4
	2	23.86	23.69	5.89	6.03	24.7	25.4
Black hickory	1	21.87	22.85	5.56	5.79	25.4	25.3
Red alder	1	25.97	25.68	2.29	5.33	20.4	20.1
	2	26.64	25.94	5.26	5.26	19.8	20.3
Bald cypress	1	35.01	33.06	4.35	3.94	12.4	11.9
	2	35.31	32.27	4.99	4.07	14.0	12.6
Eastern white pine	1	26.52	26.14	4.16	4.60	15.7	17.6
Yellow cedar	1	29.03	28.73	4.40	4.81	15.1	16.7
Southern white cedar	2	29.85	31.39	5.07	5.00	17 1	15 9
	3	32.14	32.42	5.23	5.09	16.2	15.7
Incense cedar	1	34.73	33.67	5.95	6.21	17.1	18 4

Furfural from Corncobs[1]

III—Effect of Catalysts on Furfural Yield in the Steam Digestion Process

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Laboratory experiments were made to determine the effect of employment of small amounts of catalysts. With hydrochloric, sulfuric, and phosphoric acids a marked increase of furfural yield was obtained when quantities of acid added were sufficient to neutralize the natural base of the cobs. Larger quantities did not give a proportionate increase. The effect of the mineral acids is probably due largely to the organic acids, especially formic, which are liberated. Direct addition of formic acid produced a somewhat greater increase in yield than did the mineral acids. Sulfurous acid gave results comparable with those obtained by formic acid, indicating that the presence of a reducing agent increases the yield. From an economic standpoint the sulfuric and sulfurous acid catalysts seem to offer the most promise.

Semicommercial runs using the sulfuric acid catalyst gave furfural yields of about 9 per cent, 50 per cent higher than those obtained in steam digestion without catalysts. The small amount of acid used does not require neutralization, and there is no increase in steam requirement for the process. Hence, the catalytic process offers considerable commercial advantage.

A PROCESS for producing furfural from corncobs by steam digestion and the development of this process through the semicommercial stage have been discussed in previous articles of this series.[2] The yield obtained under the optimum conditions determined was slightly over 6 per cent of the air-dry weight of cobs used, or about one-third of that theoretically obtainable.

Owing to the simplicity of the operations, low cost of the digestive agent employed, and short reaction period, furfural can be produced more cheaply by this process than by any other yet described. If the yield could be increased without material change in the conditions of the process, for instance by the addition of catalysts, even more economical production would be possible.

The catalysts first suggesting themselves were the mineral acids heretofore used in various methods for the production of furfural. The use of mineral acids as catalysts in the production of furfural from wood waste is referred to in several French patents,[3] but with no significant quantitative data. The organic acids, formic and acetic, which are by-products of the steam digestion process, also present themselves for consideration. The effect of the addition of small quantities of these agents was tested, using the apparatus and optimum conditions worked out where superheated water alone was the digesting agent.

Laboratory Experiments

Mineral Acids—The use of mineral acids, especially sulfuric and hydrochloric, for the production of furfural from pentosan-containing materials is too well known to require special mention in this article. The usual quantitative analytical method involves the distillation of the material with at least two hundred times its weight of strong hydrochloric acid, and consequently is impracticable for the preparation of furfural. Acid digestion methods described for the preparation of furfural[4] give considerably less than theoretical yields and require large quantities of reagents. The cost of such reagents, the operations necessary for their neutralization, and the special apparatus required, make such processes expensive. It seemed probable, however, that the use of very small quantities of mineral acids would result in increased yields under the conditions of the steam digestion process without involving the disadvantages mentioned.

All the catalytic experiments were made under conditions comparable with those in which water alone was the digestive agent. Except where otherwise noted the conditions were the following:

> Eight hundred grams of broken cobs are heated for 30 minutes in a copper autoclave at 180° C. with 4800 cc. of water. The temperature is held constant for 90 minutes longer while a slow distillation is maintained. The distillate collected (2700 to 3000 cc.) is measured and the furfural is determined in an aliquot part. To the weight of furfural in the distillate is added the weight of free furfural found in the liquid remaining in the autoclave and the yield is calculated from their sum. In the experiments described the catalyst was added to the water used for the charge.

The results obtained where small quantities of sulfuric, hydrochloric, and phosphoric acids were used are shown in Table I. The yields in all the tables are calculated from analysis, using the phloroglucinol method. Although they are somewhat higher than the true yield, which may be considered as slightly above 90 per cent of the values given, they are entirely satisfactory for comparative purposes.

Table I—Effect of Mineral Acid Catalysts on Furfural Yield
(Conditions: 800 grams cobs; 4800 grams water; time of digestion, 120 minutes; temperature, 180° C.)

Mineral Acid	Weight of Catalyst			Furfural Yield (Based on Air-Dry Weight of Cobs)
	Grams	Per cent of Cobs	H Equivalents	Per cent
None		..		8.9
H_2SO_4	4.0	0.50	0.08	9.8
	4.5	0.56	0.09	10.2
	6.0	0.75	0.12	10.8
	6.0	0.75	0.12	11.0
	12.0	1.50	0.25	10.9
	24.0	3.00	0.49	10.7
	80.0	10.00	1.63	7.7
HCl	2.3	0.29	0.06	10.2
	4.4	0.55	0.12	11.3
	8.8	1.10	0.24	11.8
	17.0	2.13	0.48	10.0
H_3PO_4	8.0	1.00	0.16	11.2

The addition of the acid catalysts results in a marked increase in yield. For instance, by the addition of 6 grams of sulfuric acid equal to 0.75 per cent of the weight of cobs, the average furfural yield obtained is 10.9 per cent, as compared with 8.9 per cent where water alone is used.

Several experiments were made to determine whether the presence of the small quantities of sulfuric acid used had any effect on the optimum conditions as determined for the steam digestion process. The temperature, heating period, and water-cob ratio factors were each checked up while the other conditions were kept constant. With a temperature of 170° C. a furfural yield of 7.7 per cent was obtained, as compared with 10.9 per

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[1] Received July 13, 1923.

[2] This Journal, **15**, 499, 823 (1923).

[3] Raisin, French Patent 446,871 (October 12, 1911); A. and E. Lederer, French Patent 464,608 (January 16, 1913); Classen, French Patent 518,140 (April 22, 1919).

[4] Goissedet and Guinot, French Patent 495,116 (May 8, 1917); Ricard, U. S. Patent 1,322,054 (November 18, 1919); Monroe, This Journal, **13**, 133 (1921); Adams, Conant, Clarke, and Kamm, "Organic Syntheses," Vol. I, **1921**, p. 49, John Wiley & Sons, Inc. An acid digestion method is being used for the commercial production of furfural from oat hulls by the Miner Laboratories of Chicago [*Chem. Met. Eng.*, **27**, 300 (1922)], but details of the process have not been published.

cent at the optimum temperature of 180° C. Using a 90-minute heating period (instead of one of 120 minutes), the yield was 9.8 per cent. Decreasing the volume of charge water from 4800 to 3900 cc. lowered the yield to 10.5 per cent. These experiments indicate that with small quantities of catalysts the conditions adopted for the steam digestion process give the most satisfactory results.

Phosphoric acid seems to affect the yield in about the same degree as sulfuric acid. For commercial applications the present high cost of phosphoric acid would eliminate it from consideration. Hydrochloric acid in the lower concentrations gives slightly higher yields than sulfuric acid, but when the concentration of acid is as high as 2 per cent of the weight of the cobs, the sulfuric acid catalyst gives the better yield. Of these two acids, sulfuric would probably be more economical.

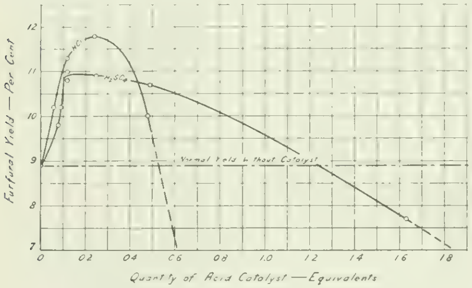

FIG. 1—EFFECT OF SULFURIC AND HYDROCHLORIC ACID CATALYSTS ON FURFURAL YIELD

By plotting the yield against the quantity of acid used, in terms of equivalents, the yield curves shown in Fig. 1 were obtained. The yield with either catalyst increases greatly with the small quantities of acid, but with the larger quantities the increase is not proportionate. In the case of sulfuric acid a quantity equal to 10 per cent of the weight of cobs causes a considerable decrease in the furfural yield.

The sulfuric acid catalyst curve (Fig. 1) has a sharp inflection at the point corresponding to 0.12 equivalent of acid (equal to $49 \times 0.12 = 6$ grams). When this or a smaller quantity of acid was employed, the liquids left in the autoclave, when tested with indicators, showed no free mineral acid. When more catalyst was used, free mineral acid was present. It may be assumed, therefore, that at the point of inflection of the curve sufficient acid has been added to correspond to the natural bases present in the cobs. This assumption was verified by an actual determination of the base. It was found that basic material calculated to be present in the ash of 800 grams of cobs corresponded to about 0.12 equivalent weight of acid.

Forty grams of cobs ashed in a platinum dish at low red heat gave 0.6000 gram of ash. The ash was warmed with a measured quantity of standard acid and the solution titrated. For neutralization of the bases present, 30.4 cc. of 0.2 *N* acid were required. The 40 grams of cobs taken therefore correspond to 0.00608 equivalent, or 0.122 equivalent weight of acid corresponds to 800 grams of cobs.

In the case of the hydrochloric acid catalyst, the curve likewise begins to flatten at 0.12 equivalent, but the peak is not reached until about 0.24 equivalent of acid is present. Beyond this point the yield decreases much more rapidly than is the case with sulfuric acid.

Apparently, where quantities of mineral acids not in excess of the quantity corresponding to the base present in the cobs are employed, their effect is chiefly due to the liberated organic acid which would otherwise be neutralized, rather than to any direct effect which they themselves may have. The quantity of organic acid ordinarily obtained in steam digestion is between 4 and 5 per cent of the weight of cobs. In one case analysis showed the organic acid to comprise acetic and formic acids, 3 and 1.4 per cent of the weight of cobs, respectively. The addition of a base would neutralize part of the organic acids and a decrease in yield might be expected. In one experiment a base in the form of sodium carbonate, in quantity equal to about 1 per cent of the weight of the cobs, was added. The resulting furfural yield was only 6.5 per cent, showing that any decrease in the free acid is disadvantageous. The quantity of base added in this case was still too small to neutralize all the acid formed in the process.

ORGANIC ACIDS—The belief that the liberated organic acid is an important factor in the increased yield obtained in the experiments described, is supported by the observations of Heuser,[5] who has shown that the quantity of furfural produced on heating xylose under pressure with water is materially increased in the presence of a mixture of acetic and formic acids. He infers that the same effect may be obtained in the case of pentosan-containing materials. Several experiments were made to test the effect of these acids as catalysts in the steam digestion of corncobs, and the data obtained are given in Table II.

TABLE II—EFFECT OF ORGANIC ACID CATALYSTS ON FURFURAL YIELD
(Conditions: Same as for Table I)

ORGANIC ACID	WEIGHT OF CATALYST Grams	WEIGHT OF CATALYST Per cent of Cobs	Furfural Yield (Based on Air-Dry Weight of Cobs) Per cent
None	..	...	8.9
Acetic	16	2.0	9.0
	20	2.5	9.4
Formic	15	1.9	12.0
	40	5.0	11.1
Acetic plus Formic	(24) (11)	(3.0) (1.4)	9.8

Experiments using quantities of acetic acid varying from 2 to 2.5 per cent of the weight of cobs produced only slight increases in yield. Thus, a furfural yield of 9.4 per cent was obtained in the presence of 2.5 per cent of acetic acid, as compared with 8.9 per cent where water alone was used.

On the other hand, formic acid produced a striking increase in yield. By using 15 grams of acid to 800 grams of cobs (slightly less than 2 per cent of the weight of cobs) a furfural yield of over 12 per cent was obtained. Larger quantities of this acid do not seem to improve the yield, which was only 11.1 per cent when 5 per cent of formic acid was used.

A much smaller quantity of added formic acid than that indicated above will produce nearly as large a yield if a quantity of sulfuric acid equivalent to the base present in the cobs is added at the same time. In one case the employment of 5 grams of formic acid (0.63 per cent) with 6 grams of sulfuric acid gave a yield of 11.7 per cent. From a practical standpoint, however, it would not be economical to use even this smaller quantity of formic acid.

When a combination of acetic and formic acids was added in quantities equal to that normally produced in the steam digestion process—3 per cent and 1.4 per cent, respectively—a 9.8 per cent yield of furfural was obtained. This experiment suggests the possibility, in large-scale practice, of using the mixture of dilute organic acids produced as a by-product in one digestion as part of the charge in subsequent digestions. In this way an appreciable quantity of formic acid could be made available economically.

REDUCING AGENTS—The results obtained indicate that formic acid plays an important role as a catalyst in the production of furfural. Since its effect is apparently different from that of other acids, the question arises if, in addition to its acidity, some other property is not partly responsible for its action. Formic acid differs from the other acids mentioned in that it is a reducing agent, and as such might protect the furfural from oxidation and accompanying polymerization during the digestion process.

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[5] *Z. angew. Chem.*, **27**, 654 (1914).

Since from an economic standpoint formic acid seemed to be unsuitable as a reducing catalyst, consideration was given to the use of a cheaper agent, such as sulfur dioxide. Experiments employing various quantities of this reagent were made. The results obtained are shown in Table III. In all cases sulfuric acid also was added in quantities sufficient to neutralize the natural base of the cobs, and the yields observed must be compared with the yield (about 10.9 per cent) obtained with the sulfuric acid alone. The addition of sulfur dioxide in quantities up to the point where about 2.4 per cent of SO_2 is present results in increased yields of furfural. At this point the yield is 12.3 per cent, or an increase of 1.4 per cent. Larger quantities of sulfur dioxide cause a decrease in yield, as shown in the table. This observation is in agreement with the fact that comparatively little furfural results from the treatment of pentosan-containing woods by the sulfite process. Since the cost of sulfur dioxide is low, it might be feasible to employ it as a catalyst in the commercial manufacture of furfural.

TABLE III—EFFECT OF COMBINED SULFURIC AND SULFUROUS ACIDS ON FURFURAL YIELD

(Conditions: Same as for Tables I and II)

CATALYST		Proportion of SO_2 to Cobs	Furfural Yield (Based on Air-Dry Weight of Cobs)
Grams H_2SO_4	Grams SO_2	Weight, Per cent	Per cent
6	..	..	10.9
6	8	1.0	11.6
6	19	2.4	12.3
6	40	5.0	10.0

MISCELLANEOUS CATALYSTS—Several neutral salts of the inorganic acids were tried as catalysts. Of these, sodium sulfate and zinc chloride in small quantities had no effect, while sodium bisulfite decreased the yield.

The adverse effect of iron in the steam digestion process has been mentioned in a previous article.[6] In cases where sulfuric acid in quantity equivalent to that of the base was employed, a similar decrease in furfural yield in the presence of iron was observed. Thus, when a sheet-iron lining was placed in the autoclave, no other change being made in the conditions, the yield was 7.9 per cent instead of 10.9 per cent.

CONCLUSIONS FROM LABORATORY EXPERIMENTS—The yield of furfural may be materially increased by adding to the charge a quantity of sulfuric acid equivalent to the quantity of the natural base of the cobs. This change is entirely practicable, since the cost of the acid would be negligible. Moreover, it is not necessary to neutralize the acid. It very quickly combines with the base of the cobs, so that its effect on the equipment would be slight. The use of formic acid, except where the dilute acid solutions produced in the process are utilized, is excluded for economic reasons. Sulfur dioxide also seems to offer some promise as a catalyst.

SEMICOMMERCIAL RUNS

The laboratory experiments having indicated that sulfuric and sulfurous acids were the most promising catalysts in increasing furfural yield, the next step was to extend the work to a semicommercial scale. Since the special equipment which would be required in the use of sulfurous acid was not available, experiments were limited to tests with sulfuric acid. The runs were made at the Bureau of Chemistry experimental plant, fully described in a previous article.[6]

A charge of 200 to 250 pounds of cobs and four times that weight of water is heated in a steel digester by means of direct steam. During the heating period a slow distillation is maintained. At the end of 2 hours the contents of the digester are discharged, and the solid residue is drained and pressed. Most of the furfural formed in the process is found in the distillate in the form of a 2 to 3 per cent solution. The portion left in the discharge liquor is generally recovered by a separate distillation as a weak solution and is added to a subsequent charge. The furfural is separated from the digester distillate by means of a specially designed column still.

The conditions found most suitable for the steam digestion process are a temperature of 180° C., corresponding to 130 to 135 pounds of steam pressure, and a digestion period of 2 hours. The yield of furfural actually isolated is slightly over 6 per cent of the air-dry weight of cobs used. The same conditions were adopted for the runs in which sulfuric acid was used as a catalyst. The data obtained are given in Table IV.

In three of the runs (2, 4, and 5) sulfuric acid, in quantity equivalent to the natural base of the cobs in the charge, was employed. This quantity is equal to 0.75 per cent of the air-dry weight of the cobs. In Run 3, instead of sulfuric acid, an equivalent quantity of sodium bisulfate was used. The yields given in the table were calculated from analysis of the distillate and discharge liquors. For comparison, data are given for a typical run where no acid was used (Run 1).

The use of the sulfuric acid catalyst increased the yield from 6.4 per cent to an average of 9.6 per cent, approximately a 50 per cent increase. The bisulfate did not seem to be quite as efficient as the sulfuric acid.

The discharge liquor showed no free mineral acids when tested with indicators and no effect of the acid on the digester was noted. Since no neutralization is required, it is entirely feasible to employ quantities of acids of the order mentioned. By using 0.75 per cent of sulfuric acid an increase in furfural yield equal to 3.2 per cent of the weight of cobs was obtained. In other words, a gain of 4.2 pounds of furfural results from the addition of 1 pound of catalyst.

Runs 1, 4, and 5 were made after the digester and steam line had been insulated with an asbestos-magnesia covering, while Runs 2 and 3 were made without this improvement. Runs 4 and 5, where the acid catalyst was used, may therefore be considered as typical from the standpoint of steam consumption, as well as from that of yield.

The steam consumption per unit weight of cobs is, of course, the same with or without the presence of the catalyst.

The steam required for the digestion in any particular run may be calculated by subtracting the quantity of charge water from the sum of the distillate and discharge liquor weights. In the table the values from Runs 4 and 5 are essentially the same as those in Run 1. The quantity of steam necessary to recover the furfural from the discharge liquors and to rectify the digester distillate will be practically the same for all runs since the vol-

TABLE IV—EFFECT OF CATALYST[a] ON FURFURAL YIELD IN SEMICOMMERCIAL RUNS

	WEIGHT OF CHARGE		Time for Heating to 180° C.	Time of Digestion	Time of Blow-Off (Pressure, 135–5 Lbs.)	Weight of Total Distillate	FURFURAL IN DISTILLATE		Discharge Liquor	Furfural in Discharge Liquor	Total Furfural Produced	Yield (Based on Air-Dry Weight of Cobs)
Run	Cobs Lbs.	Water Lbs.	Min.	Min.	Min.	Lbs.	Concentration Per cent	Weight Lbs.	Lbs.	Lbs.	Lbs.	Per cent
1	225	700	11	120	20	731	1.69	12.3	757	2.0	14.3	6.36
2	215	560	13	120	23	735	2.49[b]	18.3	993	2.5	20.8	9.67
3	214	570	10	120	20	798	2.16	17.2	961	1.7	18.9	8.83
4	224	700	10	120	19	702	2.62	18.4	827	2.8	21.2	9.46
5	229	650	8	120	20	803	2.49	20.0	820	2.3	22.3	9.74

[a] Run 1 is a typical steam digestion run without catalyst. In Runs 2, 4, and 5 sulfuric acid equal to 0.75 per cent of the weight of cobs was added. In Run 3 an equivalent amount of sodium bisulfate was used.

[b] By repeated fractionation in glass of an aliquot of the distillate the amount of furfural actually isolated was equivalent to 2.31 per cent, or 92.8 per cent of the analytical value. From this the actual furfural yield for the run is calculated to be 8.97 per cent.

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[6] THIS JOURNAL, **15**, 823 (1923).

umes and concentrations of the liquids handled do not vary materially.[7]

Because of the increased yield, considerably less steam per pound of furfural would be required in the catalytic process.

It has already been shown that the presence of iron decreases the yield of furfural, whether acid is used or not. The semicommercial experiments with the steel digester gave yields lower than those obtained under comparable conditions in the laboratory. It would seem to be advisable in commercial practice, therefore, to employ a digester lined with tile or other inert material. With this improvement it is probable that the yields would closely approach those obtained on a small scale.

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[7] For further data on steam consumption in furfural production see THIS JOURNAL, **15**, 823 (1923).

Preparation of Dicyanodiamide from Calcium Cyanamide[1]

By H. C. Hetherington and J. M. Braham

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This investigation includes a study of the most efficient method for extracting the cyanamide nitrogen from commercial calcium cyanamide, and the determination of the optimum conditions as to temperature and time of treatment for effecting the conversion to dicyanodiamide. The precautions which should be observed in the various steps of the process, and the type of equipment required have been ascertained.

From this investigation it appears that dicyanodiamide can be produced in quantity at a cost not greater than that of many organic compounds which are now used in bulk.

The solubility of dicyanodiamide in water, ethyl alcohol, and ether was also determined.

THE growing interest in the possibilities of dicyanodiamide as a base material in the synthesis of a variety of nitrogen compounds warrants further study of methods for its preparation. Its possibilities have not as yet been fully determined, but it is believed that when it becomes available in quantity at a low price its field of usefulness will be greatly extended.

The source of dicyanodiamide, commercial calcium cyanamide, is already a relatively cheap material, and hence it is in the method of producing dicyanodiamide from it that a decided lowering in cost is to be expected. The production of dicyanodiamide has formed the subject of several patents and other publications, but the literature on this subject does not contain sufficient information to enable one to carry out the process in an efficient manner. The purpose of the investigation here reported was to obtain the information necessary for the development of a process on a technical scale. In addition to laboratory studies, some larger scale experiments were performed, in the course of which 200 pounds of dicyanodiamide were prepared.

The preparation of dicyanodiamide from calcium cyanamide is based on the fact that in a hot alkaline solution cyanamide polymerizes quite readily to dicyanodiamide. Dicyanodiamide can therefore be obtained simply by extracting crude calcium cyanamide with hot water and evaporating the filtrate to crystallization. The principal difficulty in such a process is that cyanamide is converted to a considerable extent into compounds other than dicyanodiamide, resulting in a very low yield.

The main reaction involved in the preparation of dicyanodiamide may be briefly stated as follows. On extracting calcium cyanamide with water the normal salt is hydrolyzed to the acid salt and calcium hydroxide:

$$2CaCN_2 + 2H_2O \longrightarrow Ca(HCN_2)_2 + Ca(OH)_2$$

The acid salt is quite unstable in solution and undergoes a number of changes, depending principally on conditions of temperature and length of storage. It hydrolyzes further, yielding free cyanamide:

$$Ca(HCN_2)_2 + H_2O \rightleftharpoons 2H_2CN_2 + Ca(OH)_2$$

which then in part polymerizes to dicyanodiamide:

$$2H_2CN_2 \longrightarrow (H_2CN_2)_2$$

and in part hydrolyzes to urea:

$$H_2CN_2 + H_2O \longrightarrow CO(NH_2)_2$$

Other compounds, such as melamine, cyanourea, and ammonia, are also produced to a considerable extent when a solution of the acid salt is maintained at a high temperature. It is seen, therefore, that the main problem in preparing dicyanodiamide consists in converting a solution of calcium acid cyanamide, $Ca(HCN_2)_2$, into dicyanodiamide under such conditions that side reactions are reduced to a minimum.

Various modifications of the simple process mentioned above have been proposed which are essentially attempts to accelerate the polymerization reaction, thereby increasing the yield of dicyanodiamide. The catalytic influence of even very small quantities of ammonium hydroxide on this reaction was observed by Haag and Streckers,[2] and later a process for the production of dicyanodiamide was proposed[3] in which as much as one-half mol ammonia per mol of cyanamide is used. In this process a hot solution of calcium acid cyanamide, to which the ammonia has been added, is treated with carbon dioxide, the precipitated calcium carbonate filtered off, and the solution evaporated to the point of crystallization or dryness. The added ammonia is recovered. The use of cyanamides of the heavy metals—for example, zinc cyanamide—as catalysts was proposed by Immendorf and Kappen.[4] Neither of these processes has been developed.

That the rate of polymerization of cyanamide in aqueous solution is at a maximum when undissociated cyanamide and cyanamide ion, HCN_2^-, are present in equivalent proportions, was shown by Grube and Krüger[5] in their study on the kinetics of the polymerization reaction. They concluded that dicyanodiamide resulted from the union of the cyanamide ion, formed by the ionization of a salt such as calcium acid cyanamide, and an undissociated cyanamide molecule. The dicyanodiamide ion thus formed immediately changes, because of its extremely low ionization, to the un-ionized compound through combination with hydrogen ions present in the aqueous solution. A process based on these observations was patented[6] and an investigation on its technical application was made by Grube and Nitsche,[7] who stated that good results could be obtained by it. Results sub-

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[1] Received February 26, 1923.

[2] *Ann.*, **122**, 22 (1862).

[3] D. R. P. 252,273 (1910).

[4] D. R. P 257,769 (1911).

[5] *Z. physik. Chem.*, **86**, 65 (1913).

[6] Grube and Krüger, D. R. P. 279,133 (1913).

[7] *Z. angew. Chem.*, **1**, 368 (1914).

Table I—Extraction of Commercial Calcium Cyanamide with Water

Expt.	Proportion $CaCN_2$ to H_2O	Water Used in Washing Filter Cake Cc.	Temp. ° C.	Time Min.	Total Nitrogen Extracted %	Water-Soluble Nitrogen Extracted %	Total Nitrogen Lost as Ammonia %	Total Nitrogen Lost as Urea %
2	1:2.5	None	100	15	....	...	1.0	...
3	1:2.5	None	100	15	....	...	1.2	...
4	1:2.5	3 100-cc. portions	100	15	76.8	81.6	0.9	...
5	1:4	None	60 to 65	15	75.9	80.5	0.1	...
6	1:4	100	100	15	85.2	90.0	...	12.0
7	1:4	100	60 to 65	15	86.8	92.2	...	3.3
8	1:4	100	60 to 65	15	86.8	92.3	...	4.1
9	1:4	None	60 to 65	15	76.7	81.4	0.1	...
10	1:4	150 cc. (100 and 50)	60 to 65	15	87.3	92.8	0.1	....
11	1:4	90	60 to 65	30	87.0	92.0	...	....
12	1:4	None	60 to 65	30	77.8	82.8	...	...
13	1:4	400	60 to 65	35	89.8	95.4	...	...
14	1:4	None	60 to 65	30	60.4[a]	64.2	...	...
15	1:5	100	60 to 65	30	90.0	95.4	...	...
16	1:5	100	45 to 50	30	89.0	94.4		1.2
17	1:5	None	20	30	50.4	53.0	...	....
18	1:5	None	16	40	62.0	65.6		...
19	1:7.5	90	60 to 65	30	91.5	97.2	...	...
20	1:7.5	500	60 to 65	45	93.8	99.5	...	...

[a] Wash water from Experiment 13 used for extraction.

stantiating this theory of dicyanodiamide formation were independently presented at about the same time by Morrell and Burgen.[8] An investigation on the hydrolysis and polymerization of cyanamide made at this laboratory[9] further confirmed this ionic theory of dicyanodiamide formation, and also brought to light certain related reactions, particularly urea formation, which were not fully taken into account by Grube and Krüger in their study on the polymerization in the presence of calcium hydroxide. These will be referred to later in this paper.

In the course of the present investigation, preliminary experiments led to the conclusion that satisfactory results could best be obtained by a method based upon the ionic mechanism suggested by Grube and Krüger.[6] It was clearly shown in the experiments of Grube and Nitsche that the use of ammonium hydroxide in maintaining the desired ionic relations was fairly satisfactory from the standpoint of yields obtained, but, as was pointed out by these investigators, the recovery of ammonia would add an undesirable complication to the operation.

The use of the cyanamide of a heavy metal as a catalyst for the polymerization of cyanamide, as proposed by Immendorf and Kappen,[4] was not investigated in the present study, since the work of Grube and Nitsche[7] on zinc cyanamide had shown that it was not very satisfactory.

The essential feature of Grube and Krüger's method is that the concentration of cyanamide ion, HCN_2^-, and undissociated cyanamide, H_2CN_2, be so regulated that there is always present in solution one molecule HCN_2^- per molecule H_2CN_2. The most favorable conditions, particularly as regards temperature and time of treatment, had not previously been satisfactorily established. The effect of temperature on the course of cyanamide transformation is particularly important in this process, as will be shown later. In addition, there is very little information in the literature on the best conditions for the extraction of calcium cyanamide, and hence this operation also was studied in the present investigation.

Extraction of Calcium Cyanamide

The most efficient conditions of extracting calcium cyanamide as to quantity of water, temperature, and duration of extraction are, of course, somewhat dependent on equipment available and on the scale of operations. The aim, in general, however, is to secure as complete an extraction of nitrogen as possible with a minimum quantity of water in the shortest possible time, without the transformation of any of the cyanamide into forms other than dicyanodiamide.

The procedure in the extraction experiments was as follows:

One hundred grams of commercial calcium cyanamide were extracted with a measured volume of water in a mechanically stirred vessel for a given time at a temperature controlled to within 2.5° C. except as otherwise noted. A small variation in temperature has but slight effect on the result. At the end of extraction the slurry was immediately filtered on a Büchner funnel and the filter cake washed with a measured volume of water. The filtrate was analyzed for total nitrogen in all experiments, and in some cases urea, cyanamide nitrogen, and calcium were also determined. The evolution of ammonia was noted in all extractions made above room temperature. To determine the loss of nitrogen in this form several extractions were made in a closed system, the ammonia being carried into standard sulfuric acid by a slow current of air.

The calcium cyanamide used in these experiments contained 20.3 per cent total nitrogen, 19.1 per cent "water-soluble" nitrogen, and 19.1 per cent cyanamide nitrogen. By "water-soluble" nitrogen is meant the quantity of nitrogen extracted when 2 grams of calcium cyanamide are agitated with 400 cc. of water in an end-over-end extractor for 2 hours at approximately 25° C.

The results of the extraction experiments (Table I) show that the loss of nitrogen as ammonia is not particularly serious even at 100° C. during a 15-minute extraction, but that the loss as urea is very important at this temperature. Even at 60° to 65° C. for 15 minutes the loss is 3 to 4 per cent. The use of filter-cake wash water for subsequent extractions results in a low extraction, as is seen by comparing Experiments 12 and 14. From these results it appears that in technical operation the extraction of calcium cyanamide with about five times its weight of water at a temperature of 45° to 50° C. for 30 minutes will be found most satisfactory from the standpoint of general economy of operation. The quantity of wash water to be used will depend on the filtering equipment employed, but in the laboratory experiments a weight approximately equal to that of the calcium cyanamide was found desirable. The stirring during extraction should be very vigorous.

An average analysis of the extract obtained under the conditions just mentioned is:

	Per cent
Total nitrogen	3.58
Cyanamide nitrogen	3.31
Urea nitrogen	0.06
Dicyanodiamide nitrogen (by difference)	0.21
Calcium	2.41

from which the following approximate composition was calculated:

	Per cent
Calcium acid cyanamide, $Ca(HCN_2)_2$	7.35
Urea	0.12
Dicyanodiamide	0.32

Polymerization of Cyanamide

To establish the proper ratio (1:1) of free cyanamide to the ion, HCN_2^-, for a maximum polymerization rate, it is necessary to liberate one-half of the cyanamide, which is combined as calcium acid cyanamide. From the standpoint of availability and cost the choice is practically limited to three acids—namely, hydrochloric, nitric, and sulfuric. The calcium salts of the first two are so soluble that they would remain in the concentrated mother liquor with the other very soluble constituents. Their separation or elimination would be very difficult. The insolubility of calcium sulfate, on the other hand, makes possible an almost complete removal of the calcium from the solution. Sulfuric acid is also relatively cheap, and hence it was the only acid studied in this investigation.

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[8] *J. Chem. Soc. (London)*, **105**, 576 (1914).

[9] Hetherington and Braham, *J. Am. Chem. Soc.*, **45**, 824 (1923).

A convenient method of determining the quantity of acid required to establish the desired concentration is to titrate a sample of the extract with sulfuric acid, using methyl orange as an indicator. The extract may also be divided into two equal portions, one portion completely neutralized with sulfuric acid, and the solutions then recombined. A direct measure of the quantity of acid which must be added during the polymerization process is thus obtained.

EFFECT OF TEMPERATURE ON TRANSFORMATION OF CYANAMIDE—Preliminary experiments on the polymerization of cyanamide at temperatures above 85° C. indicated that only about 74 per cent of the nitrogen in solution was converted to dicyanodiamide. Qualitative tests showed that large quantities of urea were formed. To determine the effect of temperature on urea formation, a calcium cyanamide extract having a concentration of 21.76 grams total nitrogen per liter, and containing 0.32 gram urea nitrogen per liter, was treated with such a quantity of sulfuric acid that ionized and un-ionized cyanamide were present in the proper proportions. Aliquots of this solution were maintained at definite temperatures while the required amount of acid was introduced at a uniform rate over a period of 2 hours. The per cent of total nitrogen found in the form of urea at 55°, 70°, 80°, and 95° C. was 3.2, 8.2, 16.5, and 22.8, respectively. The effect of temperature on urea formation is therefore seen to be very pronounced. The cyanamide content of the final solutions was not determined and the ammoniacal silver nitrate test is unreliable in such solutions, but from later experiments it appears that only at the two highest temperatures was the conversion practically complete.

To determine the effect of operating at a moderate temperature two experiments were made at 60° C. using the procedure described above. The cyanamide was determined by precipitation with ammoniacal silver nitrate. Experience in this laboratory has shown that in the presence of urea and dicyanodiamide the silver cyanamide precipitate includes considerable quantities of these two compounds. To avoid errors from this source the silver precipitate was filtered off, washed, dissolved in dilute nitric acid, and reprecipitated by the addition of ammonium hydroxide. The silver in the precipitate was then determined, after thorough washing, by titration with standard thiocyanate. This method has been shown to give very accurate results even in the presence of large quantities of dicyanodiamide and urea. Urea was determined by the urease method.[10] The results are shown in Table II.

TABLE II—CONVERSION OF CYANAMIDE

CONSTITUENT	For 2 Hours: Grams per Liter of Solution	For 2 Hours: Per cent of Total Nitrogen	For 4 Hours: Grams per Liter of Solution	For 4 Hours: Per cent of Total Nitrogen
Total nitrogen	24.75	100.0	18.74	100.0
Cyanamide nitrogen	7.54	30.0	2.99	16.0
Urea nitrogen	0.76	3.7	1.57	8.4

In a further series of experiments solutions which originally contained 26.2 grams of nitrogen per liter as calcium acid cyanamide were maintained at 60° C. for 4 hours, following closely the precedure of Grube and Nitsche. In Experiments 1 and 2, hydrochloric acid was used as by Grube and Nitsche, while in Experiments 3 and 4, sulfuric acid was used for comparison. The results are shown in Table II*a*.

TABLE II*a*—CONVERSION OF CYANAMIDE

Expt.	Per cent of Total Nitrogen as: Cyanamide	Urea	Dicyanodiamide
1	13.5	5.7	80.0
2	12.6	5.9	78.2
3	15.1	3.2	79.8
4	15.4	3.1	78.2

It is evident from the data in the foregoing tables that conversion is far from complete at 60° C., even after 4 hours. In twelve other similar experiments substantially the same results as those given were obtained, and in no case at this temperature was it possible to obtain over 80 per cent conversion to dicyanodiamide in solution. The yields were determined by analysis of the solutions, using the nickel-guanylurea method. Grube and Nitsche reported dicyanodiamide yields as high as 89 per cent under these conditions. In view of these results and the known inaccuracy of the older analytical methods for dicyanodiamide, their results are apparently too high.

Owing to the comparatively slow rate of polymerization even at 60° C., it appears that operation at a higher temperature is to be preferred in spite of the increase in urea formation. In several experiments made at 80° C. for 1.25 hours, yields of dicyanodiamide corresponding to about 80 per cent were obtained. It was noted particularly that the percentage of urea formed was nearly as large in 1.25 hours as in 2 hours at 80° C.

The results of a series of experiments designed to determine the yields when operating at 75° C. or higher, are shown in Table III. The solutions used contained 28 to 30 grams of nitrogen per liter. Dicyanodiamide was determined by direct weighing of the carefully crystallized and dried product.

TABLE III—POLYMERIZATION OF CYANAMIDE

Expt.	Time Hours	Temperature ° C.	Yield—Per cent of Nitrogen in Solution Converted to Cyanamide
1	1.5	80 to 85	82.0
2	2	80 to 85	82.4
3	2	75 ± 2	86.4
4	2	75 ± 2	83.3
5	2	75 ± 2	85.2

It is seen from these results that when polymerization is carried out by fractional precipitation of calcium at 75° C. for 2 hours, about 85 per cent of the nitrogen in solution is obtained as dicyanodiamide. Of the remaining 15 per cent about two-thirds is urea.

As compared with operation at 60° C. the advantage of the higher temperature (75° C.) lies not only in the slightly better yield, but especially in the shorter time of treatment required.

To determine the suitability to larger scale operation of the process developed in the laboratory, 200 pounds of dicyanodiamide were made in batches, using 100 pounds of calcium cyanamide at a time. The procedure was as follows:

> The calcium cyanamide was extracted with approximately five times its weight of water at 45° to 50° C. for 30 minutes, the slurry filtered, the filter cake washed, sufficient 60° Bé. sulfuric acid added to combine with one-half of the calcium present, the solution raised quite rapidly to about 75° C., and the acid required for complete neutralization added at a constant rate for 2 hours, the calcium sulfate filtered off, the dilute solution concentrated until dicyanodiamide crystallized rapidly from a sample cooled to approximately 70° C., the solution then cooled, and the crystalline product separated by centrifugation.

The crude dicyanodiamide contains about 6 per cent of impurities, mainly calcium sulfate and urea, but also some melamine. A single recrystallization from water yields a product analyzing better than 97 per cent dicyanodiamide. Unfortunately, the filtering and pumping equipment available for the larger scale work were of a type quite unsuited for the purpose and hence significant data on the efficiency of the process were not directly obtainable. The results indicate, however, that the method could be adapted to large-scale operation, and that the efficiency reached in the laboratory experiments could also be attained on a large scale with suitable equipment. The experiments emphasized in particular the necessity of rapidly filtering the slurry immediately after extraction is completed, and of treating the filtrate at once with acid, since large quantities of urea are otherwise formed. This effect is readily explained by the known catalytic action of the hydroxyl ion on the hydrolysis of cyanamide.

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[10] Fox and Geldard, THIS JOURNAL, **15**, 743 (1923).

Although in the majority of experiments the acid was added at a constant rate over the 2-hour period of polymerization, it was found that by adding the acid more rapidly at first, keeping pace quite accurately with the reaction, about 75 per cent of the cyanamide had disappeared in the first 30 minutes. The remaining 25 per cent was not completely converted before 2 hours. Yields of 85 to 87 per cent were obtained in such cases, based on the determination of dicyanodiamide in solution by the nickel-guanylurea method (to be described in a later paper from this laboratory). In view of the comparatively small increase in yield by this variation in procedure and the added difficulty in plant operation of following the course of reaction closely with the addition of acid, there does not seem to be any marked advantage in this refinement.

Some loss of dicyanodiamide during concentration of the converted solutions was observed. To determine the approximate magnitude of this loss, portions of a solution such as is obtained in this process were evaporated at 100°, 80°, and 60° C., under such conditions that they were concentrated to the same volume (appearance of crystals at the highest temperature) in 1.25 hours. The loss of dicyanodiamide at the three temperatures was 3.5, 3.2, and 0.6 per cent, respectively. Maintaining a similar solution at 100° C. for 6.5 hours resulted in a loss of 8.2 per cent. The quantity of melamine present was shown by qualitative test to have increased considerably during concentration. These experiments emphasize the importance of carrying out the evaporation of dicyanodiamide solutions as rapidly as possible and at temperatures as low as practicable.

The combined and concentrated mother liquors from several experiments contained the following:

	Per cent
Total nitrogen	34.4
Cyanamide nitrogen	3.6
Urea nitrogen	3.6
Calcium	1.2
Sulfate	1.0

The solution was reduced to the consistency of a thick sirup, but all attempts to induce crystallization failed. One constituent was separated by its insolubility in alcohol, and identified as melamine sulfate. The presence of a considerable quantity of cyanourea was also shown. Since the nitrogen in the mother liquors represents approximately 15 per cent of the total nitrogen extracted, its recovery as ammonia by autoclaving would be advantageous, particularly if the manufacture of dicyanodiamide were carried out at a cyanamide autoclaving plant.

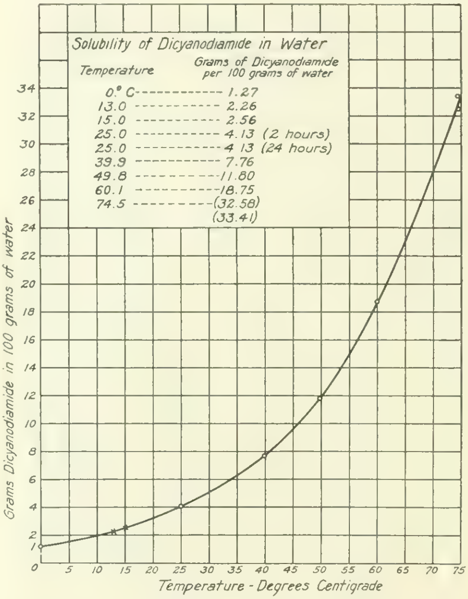
The equipment is very important in this process. Vigorous agitation during extraction, efficient filtration and washing, rather rapid evaporation of the dicyanodiamide solution, and facilities for quickly handling the solutions should be provided. The use of unprotected iron should be avoided, since cyanamide solutions are corrosive.

While an accurate cost estimate on the production of dicyanodiamide cannot be made on the basis of these experiments, there is but little doubt that dicyanodiamide can be produced in quantity at a cost well within the limits of commercial requirements.

Solubility of Dicyanodiamide in Water, Alcohol, and Ether

The solubility of dicyanodiamide in water, alcohol, and ether was determined, since there is very little information in the literature on this subject. An excess of carefully purified dicyanodiamide was mixed with the solvent in question and agitated for at least 2 hours. In one case the agitation was continued for 24 hours as a check on the shorter period. The results for the two periods were the same. Samples were withdrawn through an alundum-tipped tube, weighed, made up to definite volume, and the nitrogen was determined by the Kjeldahl method.

In Water—The results of these determinations are shown in the accompanying graph. The determinations at 13° and 15° C., represented by the crosses, were made by Pohl[11] and Werner,[12] respectively.



In Alcohol and Ether—The alcohol used in these determinations had a density of 0.7900 at 20°/4° C. (99.8 per cent); the ether had been dried over sodium and distilled. The results are shown in Table IV.

Table IV Solubility of Dicyanodiamide in Alcohol and Ether

Temperature °C.	Alcohol Grams Dicyanodiamide per 100 Grams Alcohol	Ether Grams Dicyanodiamide per 100 Grams Ether
0	0.937	0.0006
13.0	1.26[11]	0.01[1]
25.0		0.0015
26.4	1.70	...
35.0	2.26	
35.3		0.0026
49.9	3.30	....
60.1	4.13	...

The determinations in ether are not to be regarded as strictly accurate but serve to show the very low solubility of dicyanodiamide in that solvent.

Acknowledgment

The writers wish to express their appreciation of the assistance rendered by Mary A. Kelly and L. A. Pinck in the analytical work in connection with this paper.

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[11] *J. prakt. Chem.*, [2] **77**, 534 (1908).

[12] *J. Chem. Soc.* (*London*), **107**, 726 (1915).

The Analysis of Chrome-Vanadium Steel[1]

By G. E. F. Lundell, J. I. Hoffman, and H. A. Bright

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Particular emphasis is paid to the determinations which are troublesome in the analysis of chrome-vanadium steel—namely, chromium, vanadium, and manganese. The methods which are described and the observations which are recorded are largely the result of work done in the standardization of the Bureau of Standards alloy steel samples by analysts at the Bureau of Standards and in laboratories that have coöperated with the bureau.

IN THE analysis of steel works materials, where time is usually of prime importance, methods which will give the required results in the minimum of time are chosen for all determinations other than umpire analyses or primary standardization; hence, the popularity of volumetric or very simple gravimetric methods. Occasionally, these rapid methods are as accurate as the slower, long-drawn-out gravimetric ones. This is particularly true of chrome-vanadium steel where determinations of chromium, vanadium, and manganese by gravimetric methods are rare indeed and, unless extraordinary precautions are taken, not as accurate as by volumetric methods. Sulfur and phosphorus are also here generally determined volumetrically except in special work, and the results so obtained compare favorably with those obtained by gravimetric methods. Some analysts prefer to finish the direct combustion of carbon by titration or conductivity methods, but in general this element as well as silicon is weighed. It is thus apparent that the steel works analyst is quite well weaned from the balance. The following methods and observations deal therefore chiefly with accurate volumetric procedures, and are based for the most part on data obtained during the standardization of the Bureau of Standards standard samples of alloy steels.

The determinations of carbon, sulfur, and silicon in chrome-vanadium steel offer no serious difficulties, and are dismissed with references to acceptable methods and some precautions which have been found desirable. The determination of phosphorus also offers no trouble after vanadium has been reduced to the quadrivalent state, and hence no detailed descriptions of the well-known methods for phosphorus are needed. The determinations of manganese, chromium, and vanadium, on the other hand, offer some difficulties, and these are discussed at greater length and desirable methods which are not widely known are given.

Particular emphasis is placed on the methods used in the analysis of renewal No. 30*b* of the bureau's standard sample of chrome-vanadium steel. The material for this standard was furnished by the Bethlehem Steel Co., South Bethlehem, Pa., and the following firms and analysts took part in its analysis:

Bureau of Standards: The Authors, W. C. Fedde, and C. P. Larrabee
Carnegie Steel Company: Duquesne Works, W. D. Brown, Chief Chemist
Carnegie Steel Company: Homestead Works, John L. Harvey, Chief Chemist
Crucible Steel Company: C. M. Johnson, Chief Chemist
The Cleveland Twist Drill Company: A. S. Townsend, Assistant Metallurgist
Dodge Brothers: Richard B. Hooper, Chief Chemist, H. Morrison, and A. S. Anderson
Illinois Steel Company: South Works, William Brady, Chief Chemist
Ledoux and Company: G. H. Corey and L. R. Shropshire
Cambria Steel Company: H. A. Hosmer, Chief Chemist
Pennsylvania System: M. E. McDonnell, Chief Chemist
Carpenter Steel Company: E. A. Loos, Chief Chemist
Robert W. Hunt & Company: J. H. Campbell

In the analysis of the bureau's standard samples, the coöperating analysts usually employ their own laboratory methods. In addition certain constituents are determined occasionally by methods suggested by the bureau. If a reported analysis is not in close agreement with the general average, the analyst is requested to repeat the determination; the analyses listed under manganese, chromium, and vanadium are all first analyses except those in brackets, which represent successive reports by the same analyst.

CARBON

The determination of carbon presents no special difficulties, and is preferably carried out by direct combustion in oxygen and absorption in soda asbestos, as with plain carbon steel.[2]

The following precautions are worthy of special note:

1—The sample should be taken so that errors due to segregation are avoided. Neglect of this precaution is the chief source of error in careful carbon runs.

2—Blanks should be run by heating the boat and lining material in oxygen. It should be borne in mind, however, that the "blank" is the sum of plus or minus errors occasioned by such factors as: (*a*) compounds of carbon in the oxygen, boat or boat lining; (*b*) absorption or loss of water by the weighed reagents; (*c*) diffusion of oxygen from open form absorbers; and (*d*) hygroscopic changes in the weighed system. A normal blank should not run much over 0.5 mg., which represents 0.005 per cent of carbon on a factor weight (2.73 grams). It is interesting to note that a good grade of soda asbestos if used alone will lose water representing 0.01 per cent carbon on a factor weight, and that, owing to the diffusion of oxygen the open type of absorbers, such as the Midvale or Stetzer and Norton, should be weighed at equal times after the flow of gas has ceased. Tests have shown that the loss of weight approximates 0.0001 gram per 10 minutes and that complete diffusion represents approximately 0.05 per cent of carbon on a factor weight.

3—Oxides of sulfur cause positive errors approximating 0.005 per cent carbon in combustions of ordinary steels (0.04 per cent sulfur) and greater errors in high sulfur material. Consequently, steps to avoid these errors, such as using a sulfuric-chromic acid purifier, must be taken where this source of error is of consequence.

4—The burned slag should be examined for evidences of incomplete combustion and the whole combustion operation checked periodically by direct combustion of similar analyzed material, preferably Bureau of Standards steels.

First analyses for carbon in Sample 30*b* ran from 0.280 to 0.301 per cent and final analyses from 0.285 to 0.301 per cent. The maximum variation from the general average (0.292 per cent) was therefore practically ±0.01 per cent carbon. This represents the accuracy that can be expected in umpire determinations of carbon in plain and ordinary alloy steels running up to 1 per cent of carbon. In routine analyses an accuracy to ±0.02 per cent is possible.

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[1] Received May 1, 1923. Published by permission of the Director, U. S. Bureau of Standards.

[2] For detailed descriptions of this method see *Proc. Am. Soc. Testing Materials*, **22**, I, 578 (1922); also "Methods of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Alloy Steels," J. M. Camp, chairman, Pittsburgh, Pa., **1921**, p. 9.

MANGANESE

Chromium and vanadium introduce difficulties in the determination of manganese in chrome-vanadium steel, as both undergo valence changes along with manganese in many of the methods which are used for plain carbon steel. Thus, in the bismuthate–ferrous sulfate method, chromium is partially oxidized by the bismuthate and then reduced by ferrous sulfate when the reactions are performed at room temperature, while vanadium is reduced by ferrous sulfate and subsequently incompletely oxidized by permanganate when determinations are carried out rapidly in ice-cold solutions, as in methods designed to avoid interference by chromium. These troubles can be largely overcome by choosing a suitable reducing agent, such as mercurous nitrate as in Kelley's electrometric titration method,[3] or sodium arsenite as in the usual procedure.[4] All the methods, however, possess various drawbacks, as, for example, the difficult end points in procedures employing final titration with arsenite,[5] the uncertainties introduced by the precipitate and by the taking of an aliquot in the zinc oxide precipitation method, the special apparatus needed in the electrometric procedure, and the time consumed and the unpleasant fumes in the Ford method. The results obtained by the electrometric and by the Ford methods leave nothing to be desired. The following method is described because (1) it is very accurate, (2) it is reasonably rapid, (3) it does not possess disagreeable features, (4) it embodies a preliminary separation which is useful in the determination of other constituents of alloy steels, and (5) because it has not been widely published.

In this method chromium and vanadium are precipitated and separated from manganese and the most of the iron at the start. This is accomplished by dissolving the steel in dilute sulfuric acid, carefully adding sodium bicarbonate solution and then filtering. It is to be remembered that all but traces of the iron is in the bivalent state at the time of the bicarbonate addition, and that the latter is never added in sufficient amount to provide free carbonate in the solution. Similar results are achieved through the use of ammonia, as advocated by Johnson.[6] Precipitation by sodium bicarbonate or ammonia (presumably sodium carbonate or ammonium carbonate would do as well) has the advantage of introducing no troublesome reagent such as cadmium in Cain's method.[7] It is superior to precipitation by an emulsion of zinc oxide as in Volhard's method,[8] in that the method is more rapid and the quantitative separation of manganese can be made absolutely certain by a simple treatment of the precipitate. In contrast, uncertainties are introduced in Volhard's method by the volume displacement of the bulky precipitate, possible retention of manganese, and the sometimes doubtful capacities of the volumetric apparatus.

It is interesting to record that, in addition to vanadium and chromium, the bicarbonate precipitate also quantitatively holds such other constituents of alloy steel as aluminium, titanium, zirconium, cerium, and uranium, and that the precipitation separates these from the most of the iron. The bicarbonate or ammonium precipitation of these elements, therefore, quite satisfactorily serves as a rapid substitute for an ether separation. It is also a valuable aid in the detection or determination of traces of these elements in steel in that large amounts of steel can be taken; furthermore, it is superior to an ether separation where vanadium is involved, as there is no question as to the complete separation of vanadium.

BICARBONATE PRECIPITATION METHOD[9]—The success of the bicarbonate precipitation method depends on the addition of the proper amount of bicarbonate and the rapid filtration of the solution. The former can be easily controlled by attention to the preparation of the sulfuric acid solution and careful measuring of the acid. (10 cc. of 10 per cent, by volume, sulfuric acid is used up by 1 gram of pure iron, and a like volume requires 37.5 cc. of the 8 per cent bicarbonate solution.) Rapid filtration depends, of course, on the use of a good funnel and a rapid filter paper. Much quicker filtration is obtained if the precipitate is allowed to settle before filtration is attempted. In the determination of manganese, where 1 gram of sample is ample, the precipitate settles rapidly and no serious oxidation and hydrolysis of iron occurs in the covered flask during this short settling period; in bicarbonate precipitations designed to separate traces of elements like chromium and vanadium (in which 10 to 20 grams of sample and correspondingly larger amounts of acid are used), the precipitate settles less rapidly, and it is advisable to maintain a nonoxidizing atmosphere to prevent undue precipitation of iron during the settling period. Carbon dioxide is convenient for this purpose, and it is only necessary to maintain a stream of the gas over the solution sufficient to prevent back pressure.

PROCEDURE—Treat 1 gram of the sample in a 200-cc. covered Erlenmeyer flask, with exactly 20 cc. of dilute sulfuric acid (exactly 10 per cent by volume). When action is complete, dilute to 100 cc. with boiling water. Add sodium bicarbonate solution (80 grams per liter) from a buret and with gentle agitation until a permanent precipitate is formed (approximately 36 cc.) and then 4 cc. more. Again cover the flask, boil 1 minute, allow the precipitate to settle, and filter through a rapid filter, finally washing four or five times with boiling water. The filtrate contains all but traces of the manganese and will become cloudy in the funnel stem and receiving vessel, owing to oxidation and hydrolysis of the iron. This is to be expected. If the precipitation and filtration have been properly performed, there will be no more precipitate than can be conveniently handled on a 9-cm. paper. The manganese retained by the precipitate usually represents no more than 0.005 per cent. In umpire analyses or standardization this can easily be separated from chromium and vanadium and recovered as follows: Transfer the precipitate to a beaker, dissolve it in aqua regia, evaporate with sulfuric acid until fumes escape, cool, dilute, add sodium peroxide in excess, boil, filter, and wash the precipitate with hot water. Dissolve the precipitate of iron and manganese in warm, dilute 1:1 nitric acid, with the aid of a few drops of sulfurous acid if necessary, and add the solution to the original filtrate.

Remove the paper and precipitate from the funnel, and dissolve any coating in the funnel and stem in 25 cc. of warm, dilute 1:1 nitric acid, catching the solution in a small beaker. Heat the original filtrate to boiling and cautiously oxidize the iron with the 25-cc. portion of nitric acid used above. Evaporate the solution to about 25 cc., cool to 15° C., and add 1 to 2 grams of sodium bismuthate. Agitate thoroughly for half a minute, let stand for 1 to 2 minutes, add 50 cc. of 3 per cent nitric acid, and filter through asbestos. Wash with 3 per cent nitric acid until the washings run through colorless. Add 3 cc. of sirupy phosphoric acid, and titrate as usual with approximately 0.03 *N* ferrous sulfate and 0.03 *N* potassium permanganate which has been standardized against sodium oxalate.

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[3] Kelley, Spencer, Illingsworth, and Gray, THIS JOURNAL, **10**, 19 (1918).

[4] "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 25; *Proc. Am. Soc. Testing Materials*, **22**, I, 588 (1922).

[5] A word of caution in regard to the persulfate-arsenite method is here needed in that some texts call for standardization of the arsenite solution by titration against measured and acidified portions of a standard permanganate solution. This method gives titers which are too high. The correct procedure lies in first *reducing*, with sulfurous acid, the measured portion of the standard permanganate solution, and then oxidizing and titrating under the conditions that obtain in the method. As an illustration, the manganese titer of an arsenite solution was indicated as 0.000872 by the first method and as 0.000817 by the correct procedure. With another solution the titers obtained were 0.000230 and 0.000219, respectively. In the bismuthate-arsenite method the arsenite solution can be standardized directly against a standard permanganate solution.

[6] *Chem. Met. Eng.*, **20**, 523 (1919); "Chemical Analysis of Special Steels, etc.," 3rd ed., p. 362, John Wiley & Sons, Inc.

[7] *Reprint* **161** from *Bur. Standards, Bull.* I, No. **3**; THIS JOURNAL, **3**, 476 (1911); Blair, "Chemical Analysis of Iron and Steel," 8th ed., p. 199, Lippincott & Co.

[8] *Ann. Chem. Pharm.*, **198**, 318 (1879).

[9] This method originated with L. F. Witmer at the Bureau of Standards, and has recently appeared in *Proc. Am. Soc. Testing Materials*, **22**, I, 606 (1922). Sodium carbonate is used as the precipitant in a modification of this method, described in the "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 23.

The simplicity and accuracy of this procedure is demonstrated by the results obtained by a bureau analyst in his first four analyses by it. For Sample 30*b* (0.499 per cent manganese) he obtained 0.491 and 0.492 without recovery of any manganese in the bicarbonate precipitate. In Sample 30*a* the values 0.815 and 0.816 were found. In the last run the bicarbonate precipitate was analyzed and 0.005 per cent of manganese was recovered, which gave a total of 0.821 as against the value 0.822 obtained by one of the writers in the standardization of this steel.

The following results reported for renewal No. 30*b* (average value 0.499 per cent manganese) indicate the performance of different methods for manganese—bismuthate method ($FeSO_4$-$KMnO_4$ titration) after removal of chromium and vanadium as described above: 0.500, 0.504, 0.501, 0.505, 0.50, 0.496, 0.51, 0.496, 0.494 (0.483, 0.469, 0.501); bismuthate-arsenite method: 0.502, 0.488; persulfate-arsenite method: 0.51, 0.49, 0.494, 0.50; Ford-Williams method: 0.511, 0.496; Kelley's electrometric titration method: 0.505; Johnson's PbO_2-arsenite method: 0.492. In careful analyses of steels containing not more than 2 per cent of manganese, an accuracy to ±0.01 manganese can be easily obtained; in routine analyses an accuracy to ±0.03 per cent is not difficult.

PHOSPHORUS

The determination of phosphorus in chrome-vanadium steel is complicated by vanadium, which, when in the quinquivalent state, seriously retards the complete precipitation of the phosphomolybdate and contaminates the precipitate which is formed. Fortunately, the remedy is simple, as vanadium can be easily reduced to the quadrivalent condition in which it retards the precipitation of phosphorus much less and does not contaminate the precipitate if the precipitation is carried out at 15° to 25° C.[10] After these simple modifications the analysis is finished as in plain carbon steel; final weighing as magnesium pyrophosphate is the only suitable method for standardization purposes and the alkalimetric method meets all requirements as a routine method.[11] The following precautions are emphasized:

1—After the solution of the steel has been prepared as in plain carbon steel methods, it must be cooled to 15° to 25° C. and the vanadium reduced by the addition of a solution of ferrous sulfate and a few drops of sulfurous acid.

2—The precipitation of the phosphomolybdate must take place at 15° to 25° C., and at least 30 minutes must be allowed for complete precipitation.

3—In gravimetric determinations as magnesium pyrophosphate, it is desirable to use double the amount of molybdate reagent usually employed and to precipitate for a longer period, usually overnight. When the phosphomolybdate is dissolved in ammonia, small amounts of insoluble ferric phosphate may be left on the filter; therefore the paper should be finally washed with a little warm, dilute hydrochloric acid. Arsenic must be eliminated before the final precipitation with magnesia mixture[12] and ammonium citrate must be present during this precipitation, in order to prevent contamination of the precipitate by iron, chromium, or vanadium.

4—In volumetric determinations by the alkalimetric method, it is desirable to standardize the alkali solution against chrome-vanadium steel of known phosphorus content. The use of a phosphorus titer based on standardization by means of the bureau's standard benzoic acid and the use of a 23 : 1 ratio gave excellent results with Sample 30*b*.

The following results reported for renewal No. 30*b* (average 0.024 per cent phosphorus) indicate the performance of the different methods for phosphorus—alkali molybdate method with preliminary reduction of vanadium: 0.024, 0.024 (0.022, 0.024), 0.023 (0.021, 0.024), (0.022, 0.026), 0.026 (0.021, 0.023); gravimetric method (weighed as magnesium pyrophosphate after elimination of arsenic): 0.024, 0.024, 0.026. In umpire analyses of steels containing not more than 0.15 per cent of phosphorus an accuracy to ±0.002 per cent should be obtained by weighing as magnesium pyrophosphate, and ±0.003 per cent by volumetric or other gravimetric methods. In routine analyses an accuracy to ±0.005 per cent is easily achieved.

SULFUR

The accurate determination of sulfur in chrome-vanadium steel must be made gravimetrically, as with plain carbon steel, by precipitation as barium sulfate after solution of the steel in nitric acid (specific gravity, 1.42), repeated evaporation with hydrochloric acid, and reduction of the iron to the bivalent state. Very satisfactory rapid determinations of sulfur are possible by the evolution method.[13] The following notes are worthy of mention:

1—The precipitation of barium sulfate should be carried out in solutions containing not more than 1 to 2 per cent by volume of hydrochloric acid, and having the iron preferably in the ferrous condition. Higher acidity or the presence of ferric iron causes low results; errors due to the latter usually correspond to 0.001 to 0.002 per cent of sulfur.

2—The washing of barium sulfate precipitates obtained in steel analyses causes losses of the order of 0.001 to 0.003 per cent of sulfur. These can be eliminated by working over the washings.

3—Meineke's method[14] gave excellent results in the analysis of Sample 30*a*. The method now used differs somewhat from that described in the original article. It consists in dissolving the steel in copper-potassium chloride solution, filtering to separate the carbonaceous matter which contains the sulfur, destroying the carbon and oxidizing the sulfur by treatment with concentrated nitric acid saturated with bromine, eliminating the nitric acid by the addition of a little sodium carbonate followed by evaporations with hydrochloric acid, and finally precipitating with barium chloride in a solution containing 1 per cent by volume of hydrochloric acid.

4—Results by the evolution method with attack by dilute hydrochloric acid (1 : 1) and the use of an empirical titer obtained by titration of similar standard steel were excellent. The use of the theoretical sulfur titer of the iodine or iodate solution obtained from the Bureau of Standards standard sodium oxalate through permanganate and thiosulfate solutions, gave slightly low values on Sample 30*b* in the hands of the coöperating analysts (0.029 instead of 0.032 per cent sulfur). The bureau chemists, on the other hand, obtained excellent results (0.031 per cent as compared with the gravimetric value 0.032 per cent sulfur).

First analyses for sulfur in No. 30*b* (average value 0.032 per cent sulfur) varied from 0.029 to 0.033 in gravimetric analyses and from 0.027 to 0.033 in analyses by the evolution method. The final analyses varied from 0.030 to 0.033 and from 0.027 to 0.032, respectively. For steels containing no more than 0.15 per cent sulfur, umpire analyses by the gravimetric method should not be in error by more than ±0.002 per cent. In routine analyses an accuracy to ±0.005 per cent is easily obtained.

SILICON

The determination of silicon in chrome-vanadium steel is no more difficult than in plain carbon steel.[13] The following notes are worthy of mention:

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[10] Cain and Tucker, *Bur. Standards*, *Tech. Paper* **24**; THIS JOURNAL, **5**, 647 (1913).

[11] For detailed descriptions of these methods consult the references given under carbon, and also Lundell and Hoffman, THIS JOURNAL **15**, 44 (1923).

[12] Steels which contain as much arsenic as phosphorus are not uncommon; some low-phosphorus steels contain several times as much arsenic as phosphorus.

[13] See references cited under carbon.

[14] *Z. angew. Chem.*, **1**, 376 (1888).

1—With this material the Swedish method[15]—solution in sulfuric acid, evaporation until copious fumes appear, solution of soluble salts in water, and filtration—gave accurate results and less trouble than other methods.

2—In any method the period of digestion with acid following dehydration of the silica and preliminary to filtration should be as short as possible lest silica be dissolved.

3—Treatment of the ignited and weighed silica with sulfuric and hydrofluoric acids is absolutely necessary in careful analyses.

First analyses for silicon in No. 30*b* (average value 0.212 per cent silicon) varied from 0.194 to 0.22 and the final analyses from 0.204 to 0.22. For steels containing less than 0.1 per cent silicon, umpire analyses should be accurate to ±0.005 per cent; for steels containing from 0.1 to 0.3 per cent of silicon, an accuracy to ±0.01 per cent is easily attained. In routine analyses an accuracy to ±0.01 per cent and ±0.02 per cent, respectively, should be obtained.

CHROMIUM

Practically all methods for the determination of chromium in chrome-vanadium steel depend upon the oxidation of chromium to chromate and subsequent measured reduction.[16] Various oxidants are recommended, such as persulfate,[17] permanganate,[18] chlorate,[19] lead dioxide,[20] and fusion of the ammonia precipitate with sodium peroxide,[21] or carbonate and niter[22] after a preliminary separation of most of the iron.

Ferrous sulfate is universally used as the reducing medium, and it is generally added in a measured excess which is determined by final titration with permanganate; in this way vanadium and chromium are at first both reduced, but vanadium and the excess of ferrous sulfate are alone afterwards oxidized by the permanganate. The electrometric method is an exception. Here the back titration is with dichromate and finally ferrous sulfate, and therefore chromium must be obtained by subtracting vanadium as determined separately.

In all methods except the electrometric the end point causes the most concern; this is due chiefly to the color of the reduced chromium salt (also iron in the absence of phosphoric acid) and to the slowness with which the reduced vanadium is oxidized in the cool solution which is used. Other troubles are occasioned by the presence of difficultly soluble chromium carbides, by the question of complete oxidation of the chromium, and by the necessity of completely destroying all oxidants, such as permanganic acid, chlorine, and excess persulfate, before the titration.[23] In spite of these limitations most excellent determinations are possible. The following method is given because (1) it is rapid and has proved accurate in the analysis of such steels as have been tested, (2) it permits of subsequent easy determination of vanadium in the titrated solution, and (3) the circulation of the publications in which it appears[24] is limited.

PERSULFATE OXIDATION METHOD—Transfer 2.000 grams of the sample to a 600-cc. beaker and add 60 cc. of sulfuric-phosphoric acid mixture [H_2SO_4 (1 : 1) 320 cc., H_3PO_4 (sirupy) 80 cc., H_2O 600 cc.]. Heat until all action ceases, add 10 cc. of nitric acid (specific gravity, 1.20), and boil until all carbides are dissolved and oxides of nitrogen are expelled. Add silver nitrate solution (2.5 per cent) in amount equal to 0.3 gram of salt for each 1.5 per cent of chromium present. Dilute to 300 cc. with boiling water, heat nearly to boiling, and add 8 cc. of ammonium persulfate solution (15 per cent). (The purity of the persulfate should be determined as some *reagents* do not contain 25 per cent of the reagent as against 95 per cent, which is the proper strength.) If the permanganate color does not develop, add more persulfate. When the color has developed, boil the solution for 1 to 2 minutes and then add 5 cc. of sodium chloride solution (5 per cent). Continue the boiling until the pink color has just disappeared and then boil for 5 minutes longer. If the permanganate color is not destroyed by 10 minutes' boiling, or if a precipitate of manganese oxide separates, add 1 to 5 cc. of dilute 1 : 3 hydrochloric acid, and continue the boiling of the solution as above. The total period of boiling after the addition of persulfate should not be less than 15 minutes; 30 minutes will do no harm.

Cool the solution, dilute to approximately 400 cc., and titrate for chromium as follows: Add a measured excess of standard ferrous sulfate solution (50 cc. for less than 1.5 per cent of chromium, 100 cc. for 1.5 to 3 per cent chromium, etc.) and then titrate with an approximately 0.03 *N* standard potassium permanganate solution until an end point is obtained which is permanent upon continued stirring for 1 minute. The titration must be corrected for dilution effect and color interference. In colored solutions the correction can be made (1) empirically as in the U. S. Steel Corporation methods,[25] (2) by titration of the same volume of ferrous sulfate in a solution of like volume and acidity and containing the same amount of the coloring elements in their final valency, or (3) in the final titrated solution. The last is the most convenient and satisfactory in occasional analyses, and may be performed by destroying the slight excess of permanganate which is present by boiling for 10 minutes, cooling to room temperature, and then titrating with the permanganate solution to the same end point that was taken before. The volume of permanganate here required—about 0.2 cc. 0.03 *N* solution for a 1 per cent chrome-vanadium steel such as 30*b*—is to be subtracted from the result of the first titration. The difference is then a true oxidizing equivalent of the excess of ferrous sulfate employed, and the percentage of chromium may be calculated in the usual manner from a standardization based on sodium oxalate. The final solution should be preserved for the determination of vanadium as below. Tungsten, nickel, cobalt, molybdenum, arsenic, and uranium do not interfere in the foregoing method. With tungsten steel the titration is peculiar in that the solution is dark at first, owing to some tungsten–quadrivalent vanadium compound, and then clears considerably as the end point is approached.

That the method is accurate and not troublesome is indicated by the following analyses by a bureau analyst who had never used the method before: Sample 30*b*, 1.02 and 1.02 per cent chromium as compared with the recommended value 1.03; Sample 30*a*, 1.02 and 1.02 per cent chromium as compared with the recommended value 1.02; Sample 50 (tungsten 17.56 per cent, chromium 3.61 per cent, vanadium 0.756 per cent), 3.56 and 3.69 as compared with 3.61 per cent. With Sample 50 it was found advisable to use only 0.5 gram of sample on account of the peculiar end point.

The following results reported for renewal No. 30*b* (average value 1.03 per cent chromium) indicate the performance of the different modifications of the oxidation procedure: permanganate oxidation (*a*) Johnson's method, 1.01, (*b*) Barba's method,[26] 1.05; bismuthate oxidation, 1.01; chlorate oxidation, 1.02, 1.00; fusion with peroxide, 1.03;[27] persulfate oxidation methods (*a*) unclassified, 1.00, 1.04, 1.02, (*b*) with final electrometric titration, 1.01, 1.02, (*c*) by the method described above, 1.03, 1.04, 1.02, 1.03 (1.00, 1.01), 1.01, 1.02, 1.04, 1.05, 1.02.

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[15] *Proc. Am. Soc. Testing Materials*, **22**, I, 597 (1922).

[16] An exception to this procedure is that employed in an unpublished method developed by L. F. Witmer at this bureau; in this method chromium is reduced to the divalent state in a Jones reductor and afterwards oxidized to the trivalent condition by standard permanganate.

[17] "Methods of Chemists of U. S. Steel Corporation," **1921**, p. 43; Johnson, *loc. cit.*, p. 28; Kelley and Conant, THIS JOURNAL, **8**, 719 (1916); *Proc. Am. Soc. Testing Materials*, **22**, I, 609 (1922).

[18] Johnson, *loc. cit.*, pp. 5, 21; Blair, *loc. cit.*, p. 187. Ibbotson, "The Chemical Analyses of Steel Works Materials," p. 110, Longmans, Green & Co. "Methods of Chemists of U. S. Steel Corporation," **1921**, p. 46.

[19] Am. Soc. Testing Materials, Standards, **1921**, pp. 281, 294.

[20] Blair, *loc. cit.*, p. 188.

[21] Blair, *loc cit.*, p. 184.

[22] Am. Soc. Testing Materials, Standards, **1921**, pp. 271, 279, 292.

[23] Kelley and Conant, *loc. cit.*, admirably sum up the pitfalls in this process.

[24] "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 43; *Proc. Am. Soc. Testing Materials*, **22**, I, 609 (1922).

[25] "Methods of Chemists of U. S. Steel Corporation," **1921**, p. 44.

[26] Blair, *loc. cit.*, p. 187.

[27] At this bureau it has been found practically impossible to get chromium completely oxidized to chromate by fusion, water extraction, and filtration through asbestos; consequently the water extract is always acidified with sulfuric acid, treated with nitric acid, and oxidized with silver nitrate and persulfate before the final titration.

In careful determinations of chromium an accuracy to ±0.01 per cent should be obtained with steels containing not more than 1 per cent of chromium, ±0.03 per cent for steels containing 5 per cent, and ±0.10 for steels containing 20 per cent. In the same steels the accuracy obtained in routine determinations should approach ±0.02, ±0.06, and ±0.15 per cent, respectively.

VANADIUM

Aside from the colorimetric method,[28] which is chiefly used under favorable conditions for works control, the principally used methods for the determination of vanadium are volumetric and are based on its change from the quadrivalent to the quinquivalent condition, or vice versa. The reduction of vanadium is easily performed in solutions at room temperature; its oxidation, on the other hand, does not proceed as easily and is best performed at 60° to 80° C. With acid solutions containing vanadium alone the foregoing methods are quite exact, as there is no color interference and the solution can be heated if desired. Unfortunately, unless previous separations are performed, the solutions which are encountered in steel analysis contain salts of iron and often salts of such elements as chromium and nickel, which either obscure the end point or will not permit heating of the solution. These drawbacks are not fatal in routine analyses; they are, however, troublesome in accurate analyses, especially where the amount of vanadium is low and sometimes corresponds to less of the standard solution than the blank correction.

Chief among the methods depending on measured reduction are Johnson's[29] and Kelley's.[30] The former is widely employed and depends on the reduction of vanadium by means of a standard solution of ferrous sulfate and the use of ferricyanide as an internal indicator. The chief difficulty with this method lies in judging the end point, which is complicated by the normal color of the solution and by a slight interaction between the reduced vanadium and ferricyanide which yields ferrocyanide and a consequent blue color. Aside from this, in the case of renewal No. 30*b*, an additional difficulty[31] is introduced by the abnormal amount of copper (0.13 per cent) which reacts with the indicator. Kelley's method is an electrometric titration method in which the vanadium is oxidized by nitric acid and then reduced by ferrous sulfate with back titration with dichromate and ferrous sulfate. As the oxidation of vanadium by nitric acid is not quite complete, a correction factor is employed.[32] The method yields excellent results and is free from color interference; its chief drawback lies in the apparatus required.

Campagne's method[33] is perhaps the most widely known of the measured oxidation type. Here an ether separation removes most of the iron and evaporations with hydrochloric acid serve to reduce the vanadium, which is then titrated with permanganate after evaporation with sulfuric acid to remove hydrochloric acid. In this method positive errors may be occasioned by iron reduced during the ether extraction, by organic matter from the ether, by uncorrected end points, and by titration in a hot solution in the presence of chromium. Negative errors are occasioned by the slight solubility of vanadium in ether, by incomplete reduction with hydrochloric acid, and by slight oxidation due to prolonged heating with sulfuric acid. The method of the chemists of the U. S. Steel Corporation[34] is less widely known, and is given below because it has not been described in the journals and in the writers' hands has proved to be rapid and as accurate as any of those described above, except Kelley's. The method is based on the behavior of ammonium persulfate in a *cold* acid solution containing *no* silver nitrate. Under these conditions it oxidizes ferrous sulfate but does not react with quadrivalent vanadium, permanganate, bivalent manganese, or trivalent chromium. Therefore, it is possible to reduce vanadium by an excess of ferrous sulfate, to destroy the excess with persulfate, and then to titrate the reduced vanadium with permanganate.

METHOD I—(For the Routine Determination of Vanadium) See the "Determination of Chromium" above. Use the solution employed for the determination of chromium (as given above), and add 10 cc. of approximately 0.03 *N* ferrous sulfate solution if vanadium is under 0.80 per cent, 20 cc. if the vanadium content is higher, etc. Stir the solution thoroughly, add 8 cc. of ammonium persulfate solution (15 per cent solution of the 95 per cent salt) and stir for 1 minute. Titrate with approximately 0.03 *N* permanganate solution to a definite pink color which does not fade upon continued stirring for 1 minute. As in the determination of chromium, an excess of permanganate is consumed in order to overcome the dilution effect and the color interference. If this excess was actually determined after the chromium titration, the same correction should be subtracted here. If an empirical correction is made in accordance with the U. S. Steel Corporation method, a blank must be deducted equal to 0.02 per cent plus 1.8 per cent of the chromium present. It should be noted that the effect of the blank is here reversed; it lowers the percentage of vanadium but raises the percentage of chromium. Chromium, nickel, cobalt, molybdenum, arsenic, and uranium do not interfere in the foregoing method. Tungsten does interfere and must be separated in a new sample before the method is used. The performance of this method is indicated by the following results obtained by a bureau analyst in his first four analyses by it: 0.216 and 0.216 as against the recommended value 0.215 per cent vanadium in Sample 30*b*, and 0.214 and 0.216 compared with the recommended value 0.21 per cent vanadium in Sample 30*a*.

As the foregoing methods are subject to various limitations which cast the results in doubt—often very much so in the hands of novices or where only a few hundredths of one per cent of vanadium are in question—the following method is also presented. In this method, which is a modification of that described by Cain,[35] most of the iron is eliminated by a bicarbonate precipitation as described under manganese, and the remainder of the iron, together with chromium and copper, is completely removed by dissolving the precipitate and electrolyzing with a mercury cathode in a dilute sulfuric acid solution. Cobalt and nickel are also quantitatively removed, while phosphorus, arsenic, molybdenum, manganese, aluminium, titanium, zirconium, and uranium remain with vanadium in the electrolyte. The vanadium in the electrolyte is then reduced by sulfur dioxide, titrated with permanganate, and the final solution qualitatively tested for vanadium if desired. This method is not subject to the usual interfering elements, and is well suited for purposes of primary standardization and for the isolation and identification of vanadium.

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[28] "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 50.

[29] "Chemical Analysis of Special Steels, etc.," 3d ed., p. 6, J. Wiley & Sons, Inc.

[30] THIS JOURNAL, **11**, 632 (1919).

[31] Private communication from C. M. Johnson.

[32] Willard and Fenwick in a recently published method [*J. Am. Chem. Soc.*, **45**, 84 (1923)] use a polarized bimetallic electrode system instead of the usual monometallic combination [*J. Am. Chem. Soc.*, **44**, 2516 (1922)], and titrate vanadic acid directly with ferrous sulfate because of the more sensitive end point. Complete oxidation to vanadic acid is obtained by preliminary boiling with nitric acid followed by treatment with a slight excess of potassium permanganate, and any chromate formed is destroyed by boiling with sodium perborate in acetic acid solution.

[33] *Compt. rend.*, **137**, 570 (1903).

[34] "Methods of the Chemists of the U. S. Steel Corporation," **1921**, p. 47; *Proc. Am. Soc. Testing Materials*, **22**, I, 617 (1922).

[35] *Bur. Standards, Bull.* **7**, 377 (1911); THIS JOURNAL, **3**, 476 (1911); Blair, *loc. cit.*, p. 199.

Method II—(For the Accurate Determination of Vanadium) Dissolve 2.000 grams of the sample contained in a 200-cc. Erlenmeyer flask, in 30 cc. of dilute sulfuric acid (10 per cent by volume). If the steel contains less than 0.1 per cent vanadium, use a larger sample and correspondingly more acid. When action is complete, dilute to 100 cc. with boiling water, heat to boiling, and proceed with a sodium bicarbonate precipitation as in the determination of manganese described above.

Place the paper and sodium bicarbonate precipitate in the original flask, add 20 cc. of nitric acid (specific gravity, 1.42), shake until the paper is broken up, and then add 5 cc. of sulfuric acid (specific gravity, 1.84). Heat over a free flame until fumes of sulfuric acid are given off, cool, and then add more nitric acid and repeat the heating if the organic matter has not been destroyed. Finally, cool, wash down the sides of the flask, and evaporate again until fumes of sulfuric acid appear and until it is certain that all the nitric acid has been expelled. Cool, dilute to 40 cc.,[36] neutralize the solution with ammonia, and then add 1 per cent by volume of sulfuric acid in excess. Transfer the weakly acid solution to the electrolyzing apparatus, rinsing the flask with small portions of water, and keeping the total volume of the solution down to 70 cc. The electrolysis may be performed with a mercury cathode in (1) the special modified separatory funnel described and pictured by Cain[35] and also by Blair;[37] (2) in a small beaker with sealed in platinum wire as described by Smith,[38] or (3) in an ordinary beaker with the cathode lead enclosed in a glass tube extending into the mercury. In any case the cathode lead should be imbedded in about 200 grams of mercury, and the solution electrolyzed (preferably with a stirring arrangement) using a current of 5 to 6 amperes at 6 to 7 volts. Continue the electrolysis until iron is removed as indicated by a ferricyanide test on a small drop of the electrolyte. This will ordinarily require 15 to 20 minutes if the electrolyte is stirred. When iron is absent, remove the electrolyte and wash the mercury two or three times with 25 to 30 cc. of water while the current is continued. If the electrolyte is not absolutely free from iron, the electrolysis must be continued until it is. Arsenic is the only element to be feared. The small amounts of arsenic (up to 0.02 per cent) usually present in steel may be ignored except in the most accurate work. In precise work or where large amounts of arsenic are present, the properly acidified electrolyte must be treated with hydrogen sulfide, the solution filtered, and every trace of hydrogen sulfide expelled from the filtrate before the preliminary oxidation with permanganate as above. If all hydrogen sulfide is not expelled, this oxidation gives rise to sulfur which later reacts with sulfur dioxide to yield oxidizable products which cause high and erratic values for vanadium. Add 2 to 3 cc. of dilute sulfuric acid (1 : 1), heat to 70° to 80° C., and add permanganate solution until a strong pink color appears. Pass sulfur dioxide into the boiling solution for a few minutes, or until the vanadium is reduced to the quadrivalent condition, and then a rapid stream of carbon dioxide free from oxygen until the solution is free from sulfur dioxide, as shown by bubbling the stream through a feebly acidified dilute solution of permanganate. The direct use of a solution of sulfur dioxide or of any alkali sulfite is inadmissible unless these have been freshly prepared, for after a lapse of time they contain other oxidizable bodies than sulfurous acid or sulfite. Sulfur dioxide is most conveniently used from a cylinder of the liquefied gas, or it may be obtained as wanted by heating a flask containing a solution of sulfur dioxide, or of a sulfite to which sulfuric acid is added.[39] Sulfur dioxide must, of course, be entirely removed before the succeeding titration. Cool the solution to 60° to 80° C. and titrate with 0.03 N potassium permanganate solution which has been standardized against sodium oxalate. Repeat the reduction and the titration until concordant results are obtained. The titration should be corrected by a blank determination (usually amounting to about 0.10 cc.) on a solution of like volume and acidity. The final solution may be evaporated to small volume and qualitatively tested for vanadium with hydrogen peroxide in acid solution, or with hydrogen sulfide in ammoniacal solution.

This method is not as troublesome as might appear at first sight, and is quite rapid if such facilities as an electrolyzing apparatus and cylinders of sulfur dioxide and carbon dioxide are at hand. When the mercury has become saturated with iron and chromium, a fair degree of purification can be attained in a few minutes by shaking in a separatory funnel with concentrated hydrochloric acid.[40]

The following results reported for renewal No. 30*b* (recommended value = 0.215 per cent vanadium) indicate the performance of the different methods: colorimetric method[28] (0.18, 0.21), 0.19; Johnson's method,[41] 0.22,[42] 0.20; Garratt's modification of Johnson's method,[43] 0.22; Kelley's electrometric titration method, 0.22, 0.22; Cain and Hostetter's method,[44] (0.26, 0.20), 0.20; Campagne's method,[33] 0.18, 0.19, 0.20; Blair's method[45] (final procedure as in Campagne's method), 0.22; Method I, 0.21, 0.21, 0.18, 0.20, 0.21, 0.20; Method II, 0.22, 0.21, (0.16, 0.21), 0.20.

In careful analyses an accuracy to ±0.01 per cent can be easily attained with steels containing 1 per cent of vanadium and ±0.02 per cent with steels containing 2 per cent. In routine analyses an accuracy to ±0.02 per cent in low vanadium steel and ±0.04 for 1 per cent, and ±0.06 for 2 per cent vanadium steels is to be expected.

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[36] Tungstic acid retains vanadium (about 0.01 mg. for each per cent of tungsten in the steel [Kelley, Wiley, Bohn, and Wright, This Journal, **11**, 633 (1919)]. Consequently, if any appreciable amount is present at this stage, the solution must be filtered and the washed residue dissolved in an excess of ammonia. Vanadium is then separated from tungsten by the addition of 1 g. of alum, precipitation by a slight excess of ammonia, filtration and washing. The precipitate is dissolved in hot dilute hydrochloric acid, heated with 1 to 2 cc. of sulfuric acid till fumes appear, and the solution added to the original filtrate.

[37] *Loc. cit.*, p. 200.

[38] "Electro-analysis," 5th ed., p. 62, P. Blakiston's Son & Co.

[39] W. F. Hillebrand, *U. S. Geol. Surv.*, *Bull.* **700**, 186.

[40] For more complete purification, see J. H. Hildebrand, *J. Am. Chem. Soc.*, **31**, 933 (1909).

[41] *Loc. cit.*

[42] With preliminary removal of copper.

[43] Garratt, This Journal, **4**, 256 (1912).

[44] Cain and Hostetter, *Ibid.*, **4**, 250 (1912).

[45] Blair, *loc. cit.*, p. 209.

Wearing Qualities of Shoe Leathers

Wearers of shoes need definite information on the wearing quality of leather to enable them to buy shoes economically; tanners need such knowledge to enable them to make high-grade leather and to use their raw material to the best advantage and at the lowest cost. To supply this information, the Bureau of Chemistry in 1919 began a series of experiments at various army training camps, which furnish the basis for a bulletin recently issued by the Department of Agriculture.

It was evident from these experiments that shoe uppers made from the better portions of cow-grain leathers of good quality will outwear two or more soles. Fiber soles of the kinds used were not suitable for the conditions of wear, owing principally to the fact that as soon as the soles had worn down through the stitches they frequently ripped and broke off. Imperfections, such as ripping, bulging, chipping, and breaking, were numerous in the fiber soles.

Disregarding the possibility of misfitting, a full double sole and double shank of heavy leather seems to be responsible for the wasteful excessive toe wear, as such a shoe bends but little and the weight of the body is concentrated at the extreme end of the sole, instead of being distributed over a greater area at the ball.

The serviceability of various tannages, based on a standard thickness of 9 irons, was found to be as follows: oak bark, 78 days; hemlock bark, 79 days; chestnut wood extract, 80 days; belting, 85.5 days; waxed chrome, 102 days; unwaxed chrome, 126 days; and fiber soles, 122 days. Among the outstanding indications of the experiments are the superior pliability of retanned-chrome and chrome-tanned upper leathers, certain objectionable features of fiber soles and the long wear of those that did not develop such features, the increased serviceability of rolled sole leathers, and the strikingly longer wear of chrome-tanned sole leathers, especially of the unwaxed chrome-tanned leather.

SUGGESTIONS TO AUTHORS

The booklet "Suggestions to Authors," which we recently announced was in preparation, is now ready for distribution, and copies will be mailed to those who will send a request therefor to the editor's office.

Coöperation of authors in following these suggestions will be greatly appreciated in the editorial office, and by lessening ambiguity and thus making possible more prompt publication will help to bring about better satisfaction to all concerned.

The Freezing Point-Solubility Diagram of the System Tetryl-Picric Acid[1]

By C. A. Taylor and William H. Rinkenbach

Bureau of Mines, Pittsburgh, Pa

THE freezing point curves of the binary systems of TNT-tetryl[2] and TNT-picric acid[3] have previously been determined by the writers, and the freezing point curve of tetryl-picric acid, as herein discussed, completes the series.

The method, apparatus used, and the purification of the materials employed in this work have been described in detail in the articles mentioned. The tetryl had a setting point of 128.72° C., and that of the picric acid was 121.9° C. Each was melted and cooled before being used.

Considerable difficulty was encountered in obtaining accurate check results on the same mixture in the course of the work on mixtures of tetryl and picric acid. This difficulty was found to be due to a tendency on the part of these mixtures to supercool to a remarkable degree. For example, a melt containing 50 per cent of each component cooled to room temperature without the formation of a solid phase. The cold, extremely viscous liquid so obtained remained in this state for about 10 days, although the forcing of crystallization by means of "seeding" was attempted, and it then solidified very slowly. Another melt that was constantly agitated supercooled to room temperature, began to solidify slowly after 2 hours, and caused a rise in temperature of only 2 degrees.

Molecular Percentage of				Cooling Points Found	Melting Point
Tetryl	Picric Acid	Tetryl	Picric Acid	Average ° C.	° C.
0.00	100.00	0.00	100.00	121.8	...
15.00	85.00	12.34	87.66	111.75	...
30.00	70.00	25.48	74.52	99.9	...
40.00	60.00	34.72	65.28	90.0	
45.00	55.00	39.50	60.50	84.8	85.6
47.50	52.50	41.92	58.08	81.05	
50.00	50.00	44.38	55.62	76.65	85.5
52.50	47.50	46.86	53.14	72.2	85.5
55.00	45.00	49.43	50.57		85.5
58.00	42.00	52.42	47.58	77.3	.
60.00	40.00	54.48	45.52	81.0	.
62.00	38.00	56.55	43.45	84.2	84.6
65.00	35.00	59.71	40.29	90.1	....
70.00	30.00	65.05	34.95	98.3	....
77.14	22.86	72.92	27.08	108.9	....
88.12	11.88	85.14	14.86	120.2	....
90.00	10.00	87.78	12.22	121.75	....
100.00	0.00	100.00	0.00	128.72	....

In addition to the use of cooling curves for the derivation of equilibrium data, it was found advisable to employ heating curves. These were obtained by gradually heating the previously cooled melt in the apparatus used for cooling curve work, the temperature of the bath being slightly higher than that necessary for the formation of a homogeneous solution. The rise in temperature of the melt was steady until the saturation temperature was reached, when there was a period during which the temperature of the melt remained constant.

The results obtained by the use of both cooling and heating curves are shown in the table and in Fig. 1.

Interpretation of Results

Inspection of the curve derived from the foregoing data shows a different type than TNT-tetryl and TNT-picric acid. Curves showing the lowering of the melting points of the pure components in the usual way are obtained except in mixtures containing 44 to 63 per cent tetryl. A melt containing 50 per cent of each component, for example, gave a cooling curve of the type shown in Fig. 2. The maximum temperature attained (*d* in Fig. 2) varied in individual cases from 75.6° to 81.9° C. When this same mixture was allowed to solidify and was then slowly heated, a curve (Fig. 3) indicating a melting point of 85.5° C. was obtained. The other mixtures within this concentration range gave similar results.

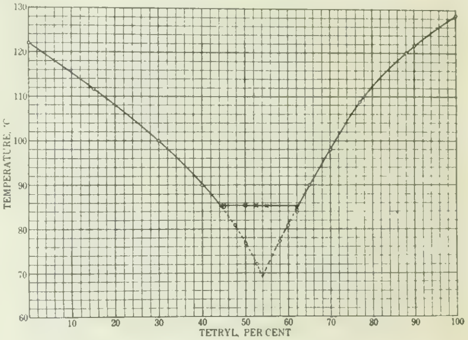

Fig. 1—Freezing Point Curve of Tetryl and Picric Acid

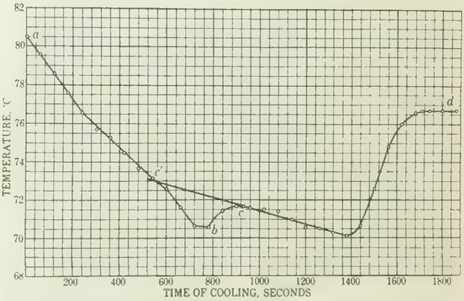

Fig. 2—Cooling Curve of Mixture of Tetryl and Picric Acid

Plotting these results (Fig. 1), we have a curve indicating the formation of a compound of the components. However, on account of the great tendency on the part of this compound to supercool, as previously shown, it was possible to complete the curve on both branches through the metastable condition.

Composition of Compound Formed

Calculation shows that the percentage composition of the simple compounds usually formed in such cases is as follows:

1 molecule tetryl	: 2 molecules picric acid	38.52 per cent tetryl
1 molecule tetryl	: 1 molecule picric acid	55.62 per cent tetryl
2 molecules tetryl	: 1 molecule picric acid	71.47 per cent tetryl

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[1] Received May 1, 1923. Published by permission of the Director, U. S. Bureau of Mines.

[2] This Journal, **15**, 73 (1923).

[3] *Ibid.*, **15**, 795 (1923).

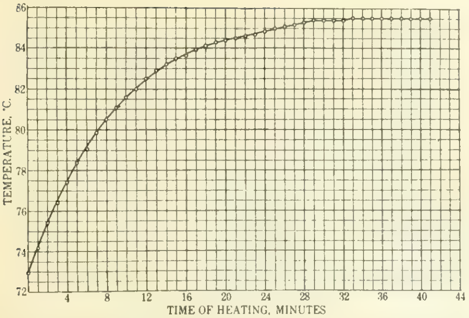

Fig. 3—Curve Showing Rise in Temperature as Mixtures of Tetryl and Picric Acid Are Heated at Uniform Rates

From this it would appear that the compound formed consists of one molecule of tetryl and one molecule of picric acid, as the others are outside the concentration range covered by the flat portion of the curve.

Melts of the pure components and various melts of these two were submitted to W. M. Myer, petrographer of the Bureau of Mines, Pittsburgh, Pa., for examination. He found that there was a third substance present in the melts, but owing to the high refractive indices of all the substances, it was not possible to make quantitative comparisons.

Application of the Data

The data can be applied to the analysis of mixtures of tetryl and picric acid in the manner described in the paper dealing with mixtures of TNT and tetryl.[2] However, it is difficult to use this method within the concentration range 44 to 63 per cent of tetryl, because of the difficulty in obtaining accurate checks and the peculiarities of this portion of the curve. The difficulty in obtaining accurate checks may be ascribed to the fact that the supercooled mixtures are rather viscous. Thick suspension of air bubbles is quickly formed when the melt is stirred, and this prevents an even rate of heat transference, so that the uneven rate of cooling under the best of conditions yields results that are not within the usual range of accuracy.

Acknowledgment

The writers wish to express their appreciation of the many helpful suggestions on the interpretation of the data given by R. E. Hall, physical chemist of the Pittsburgh Experiment Station, Bureau of Mines.

The Separation of Tin from Other Metals[1]

Including Its Determination after Precipitation by Means of Cupferron

By N. Howell Furman

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Kling and Lassieur have proposed the use of cupferron as a precipitant for quadrivalent tin. This method has been studied in detail, and found to be rapid, convenient, and accurate. It is especially suitable in connection with the analysis of tin-antimony alloys by the McCay method.

An alternate electrolytic method which Kling and Lassieur recommend highly has not been found to be satisfactory for the rapid determination of tin.

Attention has been called to a widespread serious misunderstanding of the conditions which are necessary for the separation of antimony from tin in dilute hydrofluoric acid solutions.

By means of established methods, together with some additional ones here described, tin may be separated from copper, lead, arsenic, antimony, bismuth, cadmium, zinc, manganese, cobalt, and nickel.

Nearly all the metallic elements which are commonly associated with tin in alloys—namely, cadmium,[2] copper, lead, bismuth,[2] arsenic, and antimony—may be separated completely from quadrivalent tin by precipitation with hydrogen sulfide in solutions which contain a moderate concentration of hydrogen fluoride (about 1 per cent by weight). In his comprehensive scheme of qualitative analysis, Noyes[3] made mention of the possible use of dilute hydrofluoric acid solutions of certain metals in quantitative analysis.

McCay has proved that the separations from tin are quantitative in the cases of antimony,[4] lead,[5] copper,[5] and arsenic.[6] His experiments prove that the separations are successful only when antimony and arsenic are present quantitatively in the trivalent, and tin in the quadrivalent state. Iron and zinc, if present, will be found in the filtrate which contains the tin. Preliminary results indicate that under the conditions recommended by McCay[5] in his scheme for the analysis of the tin-antimony alloys, no zinc is precipitated with the copper sulfide. This detail is being studied further.

McCay has proposed a simple and accurate method for the analysis of the tin-antimony alloys, which is based upon his excellent method for the separation of antimony from tin.[4,5] The only criticism of the original method of which the author is aware was directed toward the necessity of using a platinum dish to remove the hydrogen fluoride before a determination of tin could be made.

It was later shown by the author that the fluorine can be removed from the sphere of action by the addition of a large excess of boric acid to the solution. After the fluorine has thus been bound, perhaps in the little dissociated anion, BF_4^-, a complete precipitation of the tin as sulfide can be made in a glass vessel.[7] Alternately, it was pointed out that the tin can be deposited electrolytically after the addition of oxalic acid.[8] The current efficiency was extremely low, however, and the process was so time-consuming as to be impractical.

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[1] Received March 23, 1923.

[2] Thus far qualitative experiments only have been made in the instances of cadmium and bismuth. See Footnote 4.

[3] *Tech. Quarterly*, **16**, 93 (1903); **17**, 214 (1904).

[4] *J. Am. Chem. Soc.*, **31**, 373 (1909).

[5] *Ibid.*, **32**, 1241 (1910).

[6] *Ibid.*, **45**, 1187 (1923).

[7] Furman, *J. Am. Chem. Soc.*, **40**, 895 (1918).

[8] The details which are described in Classen-Hall, "Quantitative Analysis by Electrolysis," 5th ed., **1913**, p. 135, John Wiley & Sons, Inc., were followed.

Recently, Kling and Lassieur[9] have recommended the McCay method for the separation of antimony from tin,[4] followed by the precipitation of the tin in the filtrate by means of cupferron, after the addition of a large excess of boric acid. In a subsequent communication[10] they state that the electrolytic precipitation of the tin is to be preferred to the precipitation by means of cupferron. They have found that a complete deposition of tin may be made in 20 minutes by using a current of 4 to 5 amperes and an apparatus suitable for rapid electro-analysis. (The electrode areas were not stated, nor were any experimental results given.)

Their solutions differed from those which were previously employed by the author only in having present 2.5 grams tartaric acid, 5 to 10 grams sodium acetate, and 10 cc. concentrated hydrochloric acid, in addition to the quantities of other substances normally present.

An extended series of quantitative experiments was made in which the conditions were as closely as possible those of Kling and Lassieur. Each solution contained 0.1 to 0.25 gram tin, 5 cc. 48 per cent hydrofluoric acid, 4 to 6 grams boric acid, 5 to 7 grams ammonium oxalate, 5 to 10 grams crystallized sodium acetate, and 5 to 10 cc. concentrated hydrochloric acid (specific gravity, 1.19). The tin was introduced in the form of stanni-ammonium chloride solution containing appropriate quantities of hydrochloric acid. The total volume was between 100 and 200 cc. A current strength of 4 to 5 amperes per 100 sq. cm. cathode surface at 4 to 6 volts was employed; the speed of anode rotation was 600 to 800 per minute. In no case was the tin completely deposited in one hour. The quantities not precipitated varied from 1 to 3 mg. A further electrolysis of 1 to 2 hours under the same conditions was necessary to complete the deposition. The small quantities of tin which were not precipitated in the first hour were always recovered upon continued electrolysis with cathodes freshly plated with copper; much less than 1 mg. of tin could be easily seen under these conditions.

With stationary electrodes, employing a current of 0.5 ampere per 100 sq. cm. cathode at 3 to 4 volts, other conditions as described above, complete deposition of the tin required 20 to 24 hours. In the original experiments,[7] which were made with sulfate solutions and without sodium acetate, the time required with stationary electrodes was 40 to 48 hours, other conditions being as here described. The acceleration of the deposition is undoubtedly due to the presence of both acetates and chlorides.[11] Even with these additions, the method leaves much to be desired.

Kling and Lassieur state that the cupferron precipitation of tin is most satisfactory from the standpoint of rapidity, ease of washing, and ignition of the tin to constant weight as oxide. Inasmuch as only three test analyses were given in the two papers cited, it seemed desirable to investigate the method further, especially since these results were obtained after precipitation of the antimony from a "hydrochloric acid solution of the two metals oxidized by potassium chlorate." Such a procedure makes the separation of the antimony from tin absolutely unreliable.[12]

Numerous qualitative experiments have shown conclusively that dilute hydrofluoric acid solutions of *antimonic* compounds are very sluggishly, or not at all, affected by a rapid stream of hydrogen sulfide in one hour.[13] A new series of experiments was made in which Kling and Lassieur's directions were carefully followed. Mixtures of 0.1 to 0.3 gram each of pure tin and antimony were dissolved by 10 cc. concentrated hydrochloric acid with gradual addition of 1 to 1.5 grams of potassium chlorate. In a second series dilute hydrochloric acid (specific gravity, 1.10) was used. These solutions were neutralized with sodium hydroxide, 5 grams tartaric acid were added, and the solutions, after warming until clear and cooling, were transferred to paraffin beakers. Ten grams crystallized sodium acetate and 10 cc. 48 per cent hydrofluoric acid were added. After dilution to 300 cc. and standing for one-half hour, each solution was treated with a rapid stream of hydrogen sulfide for one hour. The amounts of antimony thus precipitated ranged from 0.6 to 54 per cent of the quantities known to be present. Presumably, these figures represent the portion of the antimony which was not oxidized by the potassium chlorate.

Abundant evidence of the presence of antimony in the filtrate was always obtained upon adding an excess of boric acid, warming the solution in a glass vessel, and again saturating it with hydrogen sulfide. The presence of a large amount of antimony sulfide admixed with the tin sulfide thus precipitated was confirmed by careful qualitative work.

A similar erroneous idea of the conditions which are necessary for the separation of antimony from tin by the McCay method is to be found in the work of Ibbotson and Aitcheson.[14]

It cannot be too strongly emphasized that the antimony must be in the lower state of oxidation in order that this separation shall be complete.

Experimental

A solution of stannic tin was prepared by dissolving about 4 grams of pure tin (the tin was of known high degree of purity, having been tested in connection with previous investigations of this series[4,5]) in 40 cc. of hot concentrated sulfuric acid. The solution was diluted to a liter after the addition of enough hydrochloric acid to prevent hydrolysis. Known portions of this solution were taken for analysis. Volumes recorded are at 20° C. The tin was precipitated as metastannic acid and weighed as oxide, following the method of Rose.[15] The following values were obtained:

Solution Taken Cc.	Tin Found Gram
25	0.1032
50	0.2062
25	0.1034
25	0.1041
Average 25	0.1034

PRECIPITATION OF TIN BY MEANS OF CUPFERRON—Numerous analytical uses of cupferron (nitrosophenylhydroxylamineammonium) have been proposed since this reagent was first introduced by Baudisch.[16] A comprehensive review of these uses has recently been made by Lundell and Knowles.[17] Marvel and Kamm[18] have studied and improved the methods of preparing cupferron. Presumably, the tin precipitate with cupferron is essentially $Sn(C_6H_5N_2O_2)_4$. Auger[19] states that he has commenced a study of the complex salts of cupferron with molybdenum, tin, and cerium; hence no attempt was made to establish the composition of the precipitate.

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[9] *Compt. rend.*, **170**, 1112 (1920).

[10] *Ibid*., **173**, 1081 (1921)

[11] Engels, *Ber.*, **28**, 3187 (1895).

[12] H. H. Willard has pointed out (private communication) that the accuracy of the tin results would not be affected since quinquivalent antimony is not precipitated by cupferron. This suggestion was studied experimentally and found to be correct. Kling and Lassieur give results which are correct for both antimony and tin.

[13] The author has made many qualitative experiments, dissolving 0.5 to 1.0 gram of pure potassium antimoniate in hydrofluoric acid (5 to 10 cc.). Upon dilution to 250 to 350 cc. and passage of hydrogen sulfide for one hour, a slight yellow coloration sometimes appears after the first half hour. Upon standing, the solution generally becomes clear in a few hours. With a deficiency of acid, however, more or less rapid precipitation of antimony may occur.

[14] "The Analysis of Non-Ferrous Alloys," 2nd ed., **1922**, p. 132. Longmans, Green & Co., has the following erroneous statement: "For this separation (i. e., antimony from tin) the metals should exist in the higher state of oxidation in hydrochloric acid solution.*** The solution *** is treated with an excess of tartaric acid and then neutralized with sodium hydrate. A solution of 48 per cent hydrofluoric acid is then added, and this is followed by an excess of sodium acetate. After diluting largely *** the antimony is precipitated by a current of sulfuretted hydrogen," etc. No more unsuitable conditions could well have been chosen!

[15] *Pogg. Ann.*, **102**, 164 (1861).

[16] *Chem. Ztg.*, **33**, 1298 (1909).

Known portions of the tin solution were taken. In a number of cases the conditions were as nearly as possible those which would be encountered in the analysis of a copper-lead-tin-antimony alloy by the McCay method—namely, 0.1 to 0.3 gram tin, 5 cc. 48 per cent hydrofluoric acid, 4 grams boric acid, 2 to 5 cc. concentrated sulfuric acid, and 5 to 10 cc. concentrated hydrochloric acid in a total volume of 200 to 500 cc.

The cupferron was added in the form of a 10 per cent solution. The solution was filtered before using. Such a solution is stable for several weeks.[20] Upon the addition of the reagent the tin precipitate separates in a white form, which is possibly an emulsion; it rapidly assumes a curdy appearance. Upon vigorous stirring in the presence of an excess of cupferron the precipitate generally passes through a stage in which it resembles superficially plastic sulfur. Finally, it becomes compact and brittle, and may be crushed to a powder with a glass rod.[21] The whole series of transformations usually requires 30 to 45 minutes. Kling and Lassieur commence the filtration when the curdy state has been reached. In this study excellent results were obtained with the brittle precipitate, the filtration being very rapid. The precipitate ordinarily has a yellowish appearance when it has become brittle and compact. There is a very noticeable clearing up of the solution when precipitation is complete. A liberal excess of cupferron is desirable.

The precipitate was washed with cold water. Precipitation and washing may easily be completed in less than an hour. After drying in a weighed crucible, the organic matter was expelled by gentle ignition. The stannic oxide was brought to constant weight in the usual manner. If the quantity of tin is larger than 0.1 to 0.3 gram, it becomes increasingly difficult to remove carbon. By breaking up the precipitate after the first ignition a rapid removal of carbon is effected.

Solutions of hydrofluoric acid to which an excess of boric acid has been added have only a slight solvent action upon glass, even on boiling. Nevertheless, those precipitates which were obtained from such solutions were tested for the presence of silica. A portion of the ignited stannic oxide was transferred to a platinum crucible and brought to constant weight. A few drops of water and dilute nitric acid, and 5 cc. 48 per cent hydrofluoric acid were added. Upon evaporation and ignition no change in weight occurred.

TABLE I—DETERMINATION OF TIN AFTER PRECIPITATION BY MEANS OF CUPFERRON

Expt.	Tin Taken Gram	Tin Found Gram	Error Mg	Total Volume Cc
1	0.1083	0.1087	0.4	300
2	0.2068	0.2066	−0.2	170
3	0.1034	0.1032	−0.2	170
4	0.1216	0.1221	0.5	400
5	0.2138	0.2142	0.4	400
6.	0.2068	0.2062	−0.6	500
7	0.1034	0.1036	0.2	250

In the first three experiments no hydrofluoric acid was present.

SEPARATION OF TIN FROM ZINC—Zinc and iron, when originally present in a tin alloy, will be found in the filtrate which contains tin in the course of the analysis by the methods mentioned.[5] Cupferron will of course precipitate the iron with the tin. The amounts of iron in tin alloys are generally small. It seems obvious that the iron oxide could be extracted from the ignited precipitate and its amount determined by a suitable method.

Experiments prove that a very satisfactory separation of tin from zinc is effected by precipitation with cupferron.

A solution of pure zinc sulfate was prepared and standardized, the zinc being weighed as pyrophosphate.

	Zinc Solution Taken Cc.	Zinc Found Gram
	25	0.1484
	50	0.2948
	25	0.1481
	50	0.2958
Average	25	0.1479

Known portions of the zinc and tin solutions were mixed. The tin was precipitated by means of cupferron, and weighed as oxide.

The determination of zinc in the filtrates was a matter of considerable difficulty. The method cannot be recommended when a rapid determination of the zinc is essential. Zinc was weighed as the pyrophosphate, either after repeated precipitations as the double ammonium phosphate, with intervening filtrations to remove organic matter, or after previous precipitation as the sulfide.

TABLE II—SEPARATION OF TIN FROM ZINC BY MEANS OF CUPFERRON

Expt.	Tin Taken Gram	Tin Found Gram	Error Mg.	Zinc Taken Gram	Zinc Found Gram	Error Mg.
1	0.1034	0.1037	0.3	0.1479	0.1491	1.2
2	0.2068	0.2069	0.1	0.1479	0.1489	1.0
3	0.1448	0.1444	−0.4	0.2958	0.2953	−0.5
4	0.1034	0.1040	0.6	0.1479	Not determined	..
5	0.1034	0.1032	−0.2	0.2958	Not determined	.
6	0.2068	0.2073	0.5	0.1479	0.1484	0.5
7	0.1034	0.1037	0.3	0.2958	0.2956	−0.2

In Experiments 2 and 6 no hydrofluoric acid was present. In these cases the filtrate was evaporated with nitric acid in order to destroy organic matter. The nitric acid was then expelled at the temperature of boiling sulfuric acid. The general conditions were similar to those of the experiments recorded in Table I.

SEPARATION OF TIN FROM MANGANESE, ZINC, COBALT, AND NICKEL—It seemed obvious that cupferron would separate tin from any or all of these metals. Solutions were prepared which contained known amounts of tin and from 0.1 to 0.15 gram each of manganese, nickel, cobalt, and zinc. Only the tin was determined.

Tin Taken Gram	Tin Found Gram
0.1034	0.1035
0.2068	0.2073

Greetings Exchanged

While the Leather Division was in session at Milwaukee, delegates from other parts of the world were already proceeding to Barcelona, Spain, to attend the international meeting of the Society of Leather Trades Chemists. In view of the unity of purpose of the two organizations, the Leather Division authorized the sending of the following message by cable:

> SOCIETY OF LEATHER TRADES CHEMISTS, CALLE URGUL 187, BARCELONA, SPAIN: The Leather Division of the American Chemical Society in congress assembled at Milwaukee sends greetings and best wishes for a successful meeting. (*Signed*) JOHN ARTHUR WILSON, Chairman.

Later the following reply was received by cable:

> The Society of Leather Trades Chemists in conference thanks the Leather Division of the American Chemical Society for its greetings and good wishes which are heartily reciprocated
>
> (*Signed*) E. SCHELL, President.

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[17] THIS JOURNAL 12, 344 (1920)

[18] *J Am. Chem Soc*, **41**, 276 (1919) A bibliography of the uses of cupferron is given.

[19] *Compt. rend*, **170**, 995 (1920).

[20] See references cited by Lundell and Knowles, *loc. cit.*

[21] Fresenius, *Z. anal. Chem.*, **50**, 37 (1911), describes a similar series of transformations of the iron salt of cupferron.

Carbon Dioxide Content of Beverages[1]

A Rapid Method for Determination of Carbon Dioxide in Lightly Carbonated Beverages

By **Joseph Cannizzaro**

113 Hudson St., New York, N. Y.

THE writer has had occasion to estimate the carbon dioxide content of beverages, especially near-beer, and has resorted to gas-volumetric and gravimetric methods such as can be found in standard books of analysis. For the most part these are either long and tedious or require one well versed with the method in order to obtain reliable results.

Of the gravimetric methods, that of Crampton and Trescot[2] was found to be the simplest and comparatively most compact. A modified form of their apparatus was used to check the results of the writer's rapid method. In principle their method consists in connecting the bottle of beverage with a standard carbon dioxide absorption apparatus and absorbing the gas in some weighed U-tubes; the difference in weight representing the carbon dioxide. This method is tedious and requires at least an hour for its proper execution, and even then the results obtained are not very reliable. Hence to an analyst who is called only once in a while to perform such an analysis its application is not very satisfactory. Obviously, the results of the gas-volumetric method are not accurate, owing to the fact that the carbon dioxide, usually collected over water, is absorbed by the latter to a considerable extent and thus vitiates the results.

The rapid method is based on the same principles as Warder's method[3] for the determination of a carbonate in the presence of a bicarbonate. It consists in quickly pipetting a definite volume of the well-cooled beverage and transferring, tip of the pipet under reagent, to a measured volume of standard sodium carbonate. The carbon dioxide reacts:

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3$$

The sodium bicarbonate being neutral to phenolphthalein at a fairly low temperature while the sodium carbonate is alkaline, the unused carbonate may be titrated with standard acid to the disappearance of the pink color, if the titrated solution is kept at about 3° to 4° C.

As carbonated beverages contain more or less fixed acid, a correction must be applied for their presence. This is easily determined on a separate portion of the sample by boiling to expel the carbon dioxide, cooling, and titrating with the sodium carbonate solution, using phenolphthalein as the indicator. The volume of sodium carbonate used is subtracted from the total volume used before in order to obtain the volume really used up by the carbon dioxide.

If the very cold beverage cannot be opened without manifest loss of gas, as indicated by excessive foaming and spilling over, this method cannot very well be applied. In the experience of the author this is of rare occurrence, especially when dealing with near-beer and other cereal beverages.

Specifically, the method found most adaptable for bottled near-beer and similar beverages is as follows:

Procedure

The beer is first thoroughly cooled by means of cracked ice and salt in a pail of suitable size. While cooling, two burets are filled, one with 0.2 *N* sodium carbonate and the other with 0.2 *N* hydrochloric acid, the latter having been standardized against the former. Thirty cubic centimeters of the sodium carbonate are then measured out in a 600-cc. beaker. This and a 25-cc. pipet are placed nearby for rapid availability. When the bottle is cold and is still surrounded by ice, it is carefully and quickly opened, without causing the least agitation to its contents, by means of a common bottle opener. The 25-cc. pipet is then quickly inserted into the bottle and the beverage carefully measured and transferred to the sodium carbonate solution, tip of the pipet below the surface of reagent. The gas is seen to be readily absorbed. The solution is then diluted to about 400 cc. with freshly boiled and cooled distilled water (to about 5° C.). One cubic centimeter of phenolphthalein indicator is then added and slowly titrated with the 0.2 *N* hydrochloric acid to the disappearance of the pink color. Twice the volume of the hydrochloric acid used is subtracted from the 30 cc. of the sodium carbonate in order to obtain the volume of the latter really used up by the carbon dioxide and fixed acids. It is clear from the reaction

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl$$

that the volume of hydrochloric acid used with phenolphthalein as the indicator is one-half the volume of the sodium carbonate present of the same normality.

To determine the fixed acids, another 25-cc. sample is placed in a 600-cc. beaker, diluted to 100 cc. and brought just to a boil, avoiding prolonged boiling. It is then cooled by placing in the cracked ice and salt bath, diluted to 400 cc. with very cold distilled water, and titrated with 0.2 *N* sodium carbonate using phenolphthalein as the indicator to the appearance of a pink color. This volume of sodium carbonate used is then subtracted from the total volume used in the first titration in order to obtain the volume of sodium carbonate used for the carbon dioxide. One cubic centimeter 0.2 *N* sodium carbonate equals 0.0044 gram carbon dioxide.

Although it is highly desirable, when opening the cold bottle containing the sample, to draw the sample in the pipet as rapidly as possible, too much suction must not be applied with the lungs, lest the pressure on the surface of the beer in the pipet be so decreased as to cause evolution of gas. The rate of drawing must be reasonably regulated. This must be kept in mind with beverages containing foaming compounds, as these have a special tendency to foam in the pipet. In such cases, provided the beverage is thoroughly cold, the foam may be disregarded and sucked directly into the mouth. After the proper volume of beverage has been drawn, it may be expectorated.

Apparently, an error is introduced in the process of transferring the sample from the bottle to the standard solution, but it is very low, well within the limits of negligence. Moreover, this minute error is inherent in every method of determining carbon dioxide in beverages, contained in bottles sealed with the so-called crown corks.

Some beverages are highly colored so that a smaller sample or a larger dilution, or both, must be employed in order to observe the end point properly.

After some practice the analyst can judge the amount of sample to use and the dilution necessary to secure a solution suitable for titration.

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[1] Received June 12, 1923.

[2] *U. S. Dept. Agr., Bur. Chem., Bull.* **107**.

[3] *Am. Chem. J.*, **3**, No. 1 (1881).

In ordinary beverages like near-beer the specific gravity may be taken as 1.025, but if the beverage is somewhat thick it is best to determine it and apply correction accordingly. The specific gravity, however, can generally be neglected in the calculation, as the error incurred is quite inappreciable.

Results and Comparison with Gravimetric Method

The results of this method have been repeatedly checked against those obtained by the Crampton and Trescot method, and the checks are reasonably within the limits of experimental error.

The following table shows eight analyses with a comparison of the gravimetric and the rapid methods:

	Per cent—Carbon Dioxide		
Sample	Gravimetric Method	Rapid Method	Difference
1	0.386	0.385	0.001
2	0.410	0.402	0.008
3	0.399	0.395	0.004
4	0.300	0.306	0.006
5	0.420	0.412	0.008
6	0.450	0.444	0.006
7	0.376	0.366	0.010
8	0.350	0.358	0.008

The first six samples were near-beer and the last two popular brands of soda water.

The same method, with slight modifications, is found in the Official Methods of the Association of Official Agricultural Chemists[4] for determining carbon dioxide in mineral waters.

[4] Assoc. Official Agr. Chem., Methods, **1920**, p. 28.

Applications of Vapor Pressure Measurements[1]

By H. S. Davis and Mary D. Davis

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A convenient vapor pressure apparatus consists of two similar glass flasks connected to a manometer tube and means whereby sealed glass containers full of liquids may be broken inside the flasks. Full details for the manipulation of such a device are given.

In the recovery of light oils from coke-oven gas by oil scrubbing, the light oil vapors are to a certain extent absorbed as a whole, and selective absorption plays a smaller part than might be expected. This fact may be partly due to differences in the rates of diffusion of the vapors, the lighter ones tending to outstrip the heavier in their race to the absorbent oil.

It is possible to check up the efficiency of a light-oil recovery plant by measuring the total partial pressure of the light oils in the gas at various points in the system, and also their tension from the absorbent oil.

In previous publications[2] the writers have described a differential vapor pressure apparatus. Further experimentation and the introduction of the device into commercial work have led to improvements in its design along the lines of durability and ease of manipulation.

Apparatus

The apparatus (Fig. 1) consists of two similar glass flasks, each with a ground-glass stopper and a capillary side tube, with stopcocks, connected to a manometer tube. Each flask is provided with a metal device whereby a small, sealed, glass container may be broken inside it. The following improvements are included in the design shown in the figure:

Manometer Tube—This was formerly connected to the flask to form one rigid piece. The writers have found, however, that joints of rubber tubing at the points shown in the figure do much to relieve strain on the apparatus, and also permit manometer tubes of different lengths to be used on the same apparatus.

Containers for Liquids—Formerly the liquid whose vapor pressure was being measured was put into small glass bulbs which were attached to movable rods so that when desired the bulb could be broken against the bottom of the flask. The containers now used are made from pieces of thin-walled tubing of 1 to 1.5 cm. outside diameter. The tubing is drawn to a capillary at one end and sealed off 1.5 cm. from the bulb. At the other end it is drawn to a somewhat larger capillary, which is cut off about 2 cm. from the bulb and left open for filling.

The metal breaking device has a holder to support the container in a vertical position inside the flask. When it is desired to release the liquid into the flask, the lower part of the breaking device is grasped with the left hand while the upper part is twisted with the right. This movement, acting on a simple contrivance, breaks off both the slender ends from the glass container and allows the liquid to flow evenly into the flask. If any trouble is encountered in breaking off the capillary ends, it may be entirely eliminated by scratching them, before filling, with a file at the desired points.

Filling the Containers—In previous descriptions detailed instructions have been given for filling small containers by alternate heating and cooling or by alternate lowering and raising of the air pressure. However, these methods are open to the following objections:

1—In the case of high-boiling liquids it is necessary to heat them so hot, in order to obtain a vapor pressure sufficient to drive the air from the bulb, that decomposition may begin. On the other hand, their vapor tensions at ordinary temperatures are so low that filling the bulb by changes of pressure is a slow process.

2—In dealing with a liquid mixture there is a tendency to fractional distillation of the liquid in the bulb.

3—Occasionally a bulb bursts through a too rapid change of pressure. Sometimes the loss of material in this way is a serious matter.

During recent investigations such methods of filling have been completely discarded and instead a capillary pipet, made by pulling out a piece of narrow tubing at one end, has been used. An outside diameter of 0.5 mm. for the capillary will enable ordinary liquids to be drawn with ease through a piece several centimeters long, and the inside diameter of the stem of the container through which it must pass need be very little larger. Such pipets made from glass tubing of 3-mm. inside diameter, and provided with a graduation mark, have been a great convenience for introducing accurate amounts of liquids into small containers of various kinds.[3]

Sealing the Containers—To seal successfully the open stem of the container, filled with a volatile liquid, it is first heated evenly in a small flame, about 1 cm. from the bulb, and drawn out to a minute capillary. The container is now put aside and allowed to cool completely, after which the capillary

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[1] Received February 12, 1923.

[2] This Journal, **10**, 707 (1918); Advisory Council for Scientific and Industrial Research of Canada, Report 2 (1918).

[3] A capillary pipet of this kind should be of great use in many physicochemical operations where it is necessary to introduce measured quantities of liquids into small glass containers which are to be sealed up afterwards in the blowpipe. For instance, measurements of vapor density in the Victor Meyer apparatus, of compressibility by certain methods, and of heats of combustion in the Bertholet bomb are made on liquids preferably after enclosing them in such containers.

end may be sealed off without disturbing the air pressure inside. Except in the case of very volatile liquids, it is not necessary or even desirable to seal off this final capillary at all, in which case the breaking device may be arranged to break off only the lower stem of the container.

QUANTITY OF LIQUID IN CONTAINER—When dealing with a homogeneous liquid such as pure benzene, the actual vapor pressure developed in the apparatus is independent of the quantity of liquid used; but in the case of a mixture of two or more liquids, the vapor pressure developed is seriously affected by this factor. This is due to the fact that the partial evaporation into the flask, which takes place after the bulb is broken, somewhat changes the composition of the residual liquid. The part which evaporates is richer in volatile constituents than the remainder, so that the final vapor tension of the residual liquid is somewhat lower than the true vapor tension of the original liquid in the bulb. This error is present in all measurements of vapor pressure by the static method. When the composition of the vapor is known, the necessary correction can easily be calculated.

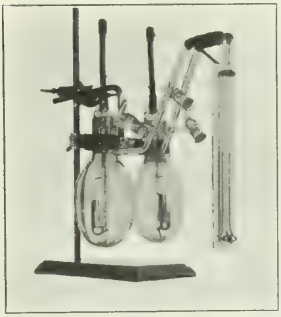

FIG 1

It will be found convenient, for all measurements of the vapor tension of liquids in this apparatus, to have the volume of liquid used one one-hundredth that of the volume of the flask.

PUTTING IN THE STOPPERS—The sealed containers are placed in the supports on the lower ends of the rods through the stoppers. The stoppers are slightly greased, put in place, and secured by small, stout rubber bands over the lugs. It is not necessary to wire in the stoppers.

WATER BATH—The flasks of the apparatus are immersed in a liquid bath until half their necks are covered, while the manometer tube remains outside.

CLEANING THE APPARATUS—After the determination is completed the stopcock in the manometer is closed, the other stopcocks are opened, and the stoppers removed. The flasks are cleaned by wiping all grease from the insides of the necks and sucking out any remaining liquid through a small glass tube connected with the suction pump. They are then rinsed with a little benzene or alcohol, which is afterwards sucked out. Between the apparatus and the suction pump there should be a small safety bottle to catch fragments of glass. Each of the flasks is then throughly cleaned of vapor by drawing air through it for at least 15 minutes in the following manner: A cork stopper, through which has been fitted a glass tube reaching nearly to the bottom, is placed in the flask. Suction is now applied to the stopcock and air is drawn in through the glass tube to the bottom of the flask and out at the stopcock.

Caution—It is of the utmost importance that the apparatus be kept clean from any liquid of the kind whose vapor pressure is being determined. The stoppers must be removed from the apparatus as soon as the experiment is completed. If they are left for long periods in the flask containing a volatile liquid, its vapor may penetrate the connecting tubes and rubber connections, causing trouble.

SPECIFIC DIRECTIONS FOR MEASURING THE VAPOR TENSION OF A LIQUID

(*a*) Fill a container with a measured quantity of liquid.
(*b*) Place it in the support attached to the right-hand stopper and insert the stoppers in the flasks.
(*c*) Put the apparatus in the water bath. Open both stopcocks to the air in order to bring the pressures in both flasks to atmospheric, then open the manometer stopcock and close the other two
(*d*) Read the manometer levels, estimating with the eye to tenths of millimeters, at 5-minute intervals until the readings are constant.
(*e*) Break the container.
(*f*) Read the manometer levels at intervals until they are constant.
(*g*) Close the manometer stopcock, open the other stopcocks, remove the stoppers, and clean the apparatus.
(*h*) Read the temperature of the bath and the barometer pressure.

The difference between the final and initial readings gives the vapor tension from the liquid in terms of the manometer liquid. If the absolute value of this pressure is desired, certain obvious corrections must be applied. The largest of these arises from changes of air pressure in the two flasks caused by the movement of the manometer liquid. This correction is of special importance when a light liquid is employed and, in some cases, may amount to 25 per cent of the total reading.

The following measurements carried out on the tension of light oil from a sample of stripped oil from a well-operated American plant will illustrate the method:

Time Min	Pressure in Millimeters of Oil (Sp. Gr., 0.86) No. 1	 No. 2
0 (Put apparatus in bath)	3.1	1.5
5	1.7	1.2
10	0.7	[illegible]
16	0.4	0.4
20	0.2	0.1
25	0.1	0.0
30 (Apparatus at equilibrium and ready for experiment)	0.0	0.0
0 (Broke bulb of oil in flask)	0.0	0.0
5	3.6	3.3
10	3.7	3.9
15	3.8	4.1
25	3.9	4.2
Pressure developed	3.9	4.2
Correction for changes in air pressures in flasks	0.9	0.9
Total pressure	4.8	5.1
Pressure in millimeters of mercury	0.30	0.32

DIFFUSION OF VAPORS AND ITS RELATION TO ABSORPTION PROCESSES

The rates at which vapors are disseminated by true diffusion and by convection currents are very different, as the following striking experiment will illustrate:

Fix firmly in one of the supports a container completely open and unrestricted at the top. Fill this with a volatile liquid to within a few millimeters of the brim and leave it unsealed. Then lower the stopper gently into place in the flask. It will be found that the development of pressure is surprisingly slow. Now break the lower stem of the container, thus allowing the liquid to flow over the bottom of the flask. The usual rapid development of pressure, caused mainly by convection currents, will result.

It is well known that the evaporation of a liquid into a gas at rest is determined principally by the rate of diffusion of its vapor through the gas which lies above it, and similar considerations must apply to the absorption of its vapor into a nonvolatile medium. It would reasonably follow that the rates at which two vapors are simultaneously absorbed from a gas into another medium must be somewhat influenced by the difference in their rates of diffusion in the gas. This difference is greater than that between their rates of diffusion separately in the gas, according to the curious law, first pointed out by Graham, that the movement of the faster is accelerated and that of the slower retarded in simultaneous diffusion.

Of course, if equilibrium were reached at each point in the absorption system, Raoult's law and the law of partial pressures would hold. On the other hand, if equilibrium is not attained, there should be a tendency for the heavier and less diffusible vapor to be retained in the gas. It will be readily seen that such an effect would oppose selective absorption.

TESTING EFFICIENCY OF BENZENE (LIGHT OIL) SCRUBBERS[3]

If selective absorption of the various light oil vapors took place to any great extent in an ordinary scrubber, then the relative proportions of the constituents of the light oil in the absorbent oil would vary at different points, the higher boiling constituents predominating in the first part of the washing system.[4]

The selective absorption effect is much less than might be expected, and perhaps this can be explained by the diffusion effect pointed out above. But whatever the explanation, the fact remains that in an ordinary light oil scrubber the benzene and toluene, to a certain extent, are absorbed, not in inverse proportion to their volatility, but as a whole. It requires prolonged contact between the absorbing medium and the gas to effect a separation of the two vapors.[5]

For this reason vapor pressure measurements can be successfully applied to the control of light oil scrubbers in the following ways:

1—The relative efficiencies of the different units can be compared by measuring the tension of light oil from samples of wash oil taken from various points in the system.

2—The measurements in No. 1 can be checked by measuring the pressure of the residual light oil in the gas at these same points.

3—The efficiency of the stripping still can be checked by measurements of the tension of light oil from the debenzeneized oil. This is an important measurement because no amount of scrubbing will ever reduce the benzene content in the gas below a pressure equal to the tension of light oil from the debenzeneized oil.

The measurement of the vapor tension of light oil from an absorbent oil is a comparatively easy matter and has already been described.

Comparative measurements of the total pressure of light oil in the gas at various points in the system are carried out in the following manner: Into each flask of the vapor pressure apparatus is put a sealed container filled with an accurately measured quantity of liquid benzene. (It is recommended that the volume of benzene used be one one-hundredth of the volume of each flask.) One flask of the apparatus is then filled with the gas to be analyzed and the other is left full of air. When the two containers are broken simultaneously, the differential pressure which develops between the two flasks is proportional to the vapor pressure of light oil originally present in the gas. The theory of these measurements has already been dealt with in previous publications.[2] The writers failed, however, to lay enough stress on the importance of measuring *equal* volumes of benzene into the containers in each experiment and of preserving the same ratio between the volumes of benzene and of the flasks in separate experiments.

In 1917 tests were carried out with this apparatus on a light oil recovery plant operating under war conditions on coke-oven gas in Canada. The absorption system comprised six large washing towers of the hurdle type in series, through which the gas and wash oil were passed in countercurrent contact. In 1918 further tests were carried out. During the intervening period centrifugal sprays had been introduced before each of the first three towers in a vain attempt to increase the recovery.

The experienced operator of a modern benzene-recovery plant will at once perceive that this was a very inefficient recovery unit, and indeed, in view of the results obtained from these tests, radical changes were planned in it which were only cut short by the armistice.

A summary of the results from these tests is given in Table I.

DISCUSSION OF RESULTS

Through the greater part of the absorbing system, the vapor tension of light oil from the wash oil was nearly equal to the partial pressure of light oil in the gas at the corresponding point. Indeed, the wash oil in the third tower actually gave up benzene to the gas, a condition which was traced to its relatively higher temperature there.

In spite of the superabundance of washing, a large part of the benzene passed through the towers unabsorbed. This condition was caused by the inefficiency of the stripping (Hirzel) still, which left a large percentage of light oil in the poor or debenzeneized oil. No amount of washing will ever compensate for inefficiency in the still.

The quality of coke-oven gas delivered to this plant varied much in quality. On May 13 the superintendent was annoyed by the small output of light oil, whereas on the 17th the yield was excellent. As will be evident from the table, these discrepancies were caused, not by any change in the efficiency of the benzene-recovery unit, but by variations in the quality of the gas.

GASOLINE AND SOLVENT RECOVERY

Many of the principles of benzene recovery are embodied in processes for the recovery of gasoline from natural gas or still vapors. There is, however, this difference, that the benzene is rather sharply defined from the other constituents of coke-oven gas in chemical and physical properties, whereas the dividing lines between the constituents of natural gas are much less clearly marked, and the properties of the gasoline are greatly influenced by the methods of recovery. However, a study of the vapor pressures involved cannot fail to throw light on any system for gasoline or solvent recovery.

TABLE I—VAPOR PRESSURE MEASUREMENTS ON THE SCRUBBING TOWERS (SIX TOWERS AND THREE SPRAYS, IN SERIES) OF A LIGHT OIL-RECOVERY PLANT

SAMPLE	LAST POINT IN SCRUBBERS PASSED BY GAS	September, 1917	May 6, 1918	May 13, 1918	May 14, 1918	May 17, 1918	May 18, 1918
Rich oil	......	...	6.1	...	...	...	.
Rich gas	Entrance	8.4	...	6.1	7.3 7.7 } 7.5	10.3 (5.3)	5.4
Gas from Tower 1	1st spray	...	7.5 6.0 } 6.8	...	7.0	(4.3)	(4.2)
Gas from Tower 2	Tower 1 (2nd spray)	6.2	5.7	...	5.2	...	...
Gas from Tower 3	Tower 2 (3rd spray)	4.6	3.1 3.0 } 3.1	...	5.0	.	.
Gas from Tower 4	Tower 3	5.0	3.5 3.5 } 3.5	...	5.0	. .	. .
Gas from Tower 5	Tower 4	4.8	3.6 3.5 } 3.5	. .	4.8	.	. .
Gas from Tower 6	Tower 5	3.7	3.0 3.6 } 3.3	...	...	.	
Poor gas	Tower 6	3.3	2.5 2.7 } 2.6	4.3	4.2	5.8 (3.9)	2.2 (2.4) } 2.3
Poor oil	From Hirzel still	. .	3.0	. .	...	. .	.

In the case of a gas, the figures represent the total partial pressures of the light oil vapors in millimeter of mercury; in the case of an oil they refer to vapor tensions of light oil in millimeter of mercury. The figures in parenthesis indicate partial pressures of pure benzene (C_6H_6).

The table shows:

1—That the light oil content of the coke-oven gas varied from day to day.

2—That no absorption was taking place in Towers 3, 4, and 5.

3—That about one-third of the light oil passed through the scrubbing system unabsorbed.

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[4] Cantello, *Can. Chem. Met.*, **6**, 196 (1922).

[5] Sperr, *Gas Age*, **41**, 393 (1918).

Preliminary Examination of Water Samples[1,2]

Calcium and Sulfate by Turbidity and Hardness by the Soap Method

By W. D. Collins and Margaret D. Foster

U. S. GEOLOGICAL SURVEY, DEPARTMENT OF THE INTERIOR, WASHINGTON, D. C.

The preliminary examination of a water sample will save time in making a complete mineral analysis, and may show that a complete analysis is not necessary. The examination will include titrations of chloride and alkalinity by the usual methods, turbidimetric determinations of sulfate and calcium by comparison with standards in test tubes, and sometimes a determination of hardness by the soap method.

The turbidimetric tests are made with volumes of 10 cc. for the sample and standards. For the sulfate precipitation 1 cc. of acid barium chloride solution is used (48 cc. of hydrochloric acid, specific gravity 1.19, and 100 grams of $BaCl_2.2H_2O$ in 1 liter). For calcium 1 cc. of acetic acid (equal parts of 99.5 per cent acid and water) is added, the solution is shaken, 1 cc. of potassium oxalate solution (0.2 gram $K_2C_2O_4$ per cc.) is added, the solution is shaken again and after 10 minutes the turbidities are compared.

Tests of one hundred seventy-four waters varying in composition over a wide range show that the preliminary results for sulfate, calcium, and hardness are reasonably close to the results obtained in the complete analysis. In general, the error is likely to be about 10 per cent of the quantity determined, and may be plus or minus. For preliminary examinations or for field work[3] this accuracy is sufficient.

IN a laboratory where samples of water received for analysis may contain from 25 to 25,000 parts per million of dissolved mineral matter, it is well worth while to make a preliminary examination before proceeding to evaporate the part of the sample that is to be used for the complete mineral analysis. The preliminary examination ordinarily involves the determination of the acid radicals present in considerable quantities and the calcium and magnesium or their equivalent. From these results it is possible to calculate the sodium needed to balance the analysis and thus have roughly a complete analysis.

In most natural waters the only acid radicals to be considered are chloride, sulfate, and bicarbonate or carbonate. Only a few waters contain enough nitrate to enter into the calculation of the quantity of sodium, or to cause the solution of platinum when the waters are evaporated with hydrochloric acid in a platinum dish. It is always well, however, to determine the nitrate before the acidified sample is evaporated. The regular methods for the titration of chloride and bicarbonate are sufficiently rapid to serve for the preliminary examination. Sulfate is the only acid radical for which a special method must be used in the preliminary examination.

The determination of total hardness of a water by the soap method gives a measure of the combined calcium and magnesium and serves as a basis for calculation of the sodium. A turbidimetric determination of calcium takes less time than a soap test and often is sufficient for determining the quantity of a sample to take for evaporation.

In order to have definite data in regard to the reliability of simple turbidimetric sulfate and calcium determinations and the soap test as applied in regular laboratory work, these three tests were made on each of a series of one hundred seventy-four samples which were analyzed in the Water Resources Laboratory of the U. S. Geological Survey over a period of about a year. The results of these tests as discussed below, and as shown in Figs. 1, 2, and 3, demonstrate the usefulness of the methods for preliminary examinations. The data show clearly that the methods as used cannot be trusted to give results that can be used in place of regular analytical determinations. If greater accuracy is desired without making a complete analysis, it can be obtained by using the rapid methods described by Hale,[4] or by using the turbidimeter in the determination of sulfate and calcium. The turbidimetric determinations described below are made without the turbidimeter and require only 10 cc. or less of the sample.

SULFATE

Estimation of quantities of sulfate by the turbidity produced on the addition of barium chloride to an acidified solution is probably one of the oldest of the simple rapid quantitative methods. A number of authors[5] have described various ways of increasing the accuracy of the turbidimetric determination of sulfate, and it is probable that in many laboratories where large numbers of routine sulfate determinations are made the results obtained with the turbidimeter are as accurate as gravimetric results. Such accuracy is not generally found in the results of turbidimetric determinations of sulfate in miscellaneous samples of water, nor is it necessary in preliminary examinations. Equally useful results are obtained by the simple procedure outlined below.

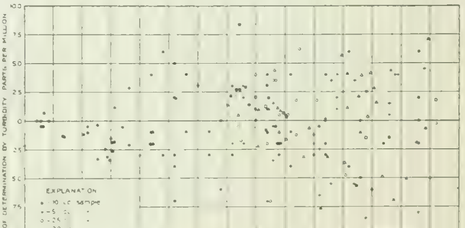

FIG. 1—ERRORS IN DETERMINATIONS OF SULFATE BY TURBIDITY

Samples of 10 cc. are taken in test tubes (100 × 10 mm.) and standards are made up containing from 0.05 to 0.35 mg. of sulfate (SO_4) in 10 cc. To each tube is added 1 cc. of an acid solution of barium chloride (48 cc. of hydrochloric acid of specific gravity 1.19 and 100 grams of $BaCl_2.2H_2O$ in 1

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[1] Received May 4, 1923.

[2] Published by permission of the Director, U. S. Geological Survey.

[3] Collins, "Field Examination of Water," special circular, U. S. Geol. Survey, March, **1922**.

[4] *J. Am. Chem. Soc.*, **29**, 1078 (1907).

[5] Hinds, *Ibid.*, **18**, 661 (1896); **22**, 269 (1900); Jackson, *Ibid.*, **23**, 799 (1901); Muer, THIS JOURNAL, **3**, 553 (1911).

liter). The tubes are shaken vigorously and the turbidities compared by looking through the depth of the liquid at a black background. If the sample contains over 35 parts per million of sulfate, a smaller portion is diluted to 10 cc. with distilled water. If the sulfate is over 700 parts per million, a dilution is made and the proper quantity of the diluted sample is taken for the determination.

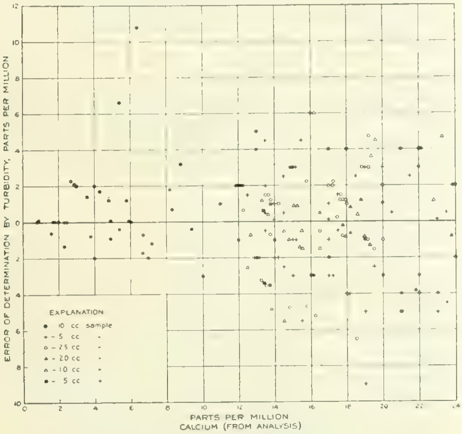

Fig. 2—Errors in Determinations of Calcium by Turbidity

Fig. 1 shows the differences between the sulfate found by the rough turbidimetric method and the quantity found by the regular gravimetric method in the course of the complete analysis. The complete analyses all balanced well enough to indicate that the differences were due almost entirely to the error of the turbidimetric comparisons. The points which represent 10-cc. samples show the actual quantity of sulfate determined by analysis plotted against the difference between this quantity and that determined by turbidity. For the points representing samples of 5 cc. the analytical result has been divided by 2 and plotted against half the difference between the gravimetric and turbidimetric results. Similar reduction has been made for the smaller samples.

The average of the percentage differences for all the samples is 16 per cent of the analytical results. For the seventy-seven samples of 10 cc. the average difference of 22 per cent corresponds to only 2.4 parts per million of sulfate (SO_4), which is of no practical significance. An average difference of 12 per cent for the fourteen samples of 0.5 cc. represents an average difference of 50 parts per million of sulfate, which is considerably more than the allowable error in the gravimetric determination of from 350 to 700 parts per million of sulfate. The turbidimetric determination of sulfate in test tubes is thus shown to be sufficiently accurate for a preliminary examination of a water sample, but not reliable enough to take the place of a gravimetric determination. It calls for no special apparatus, is rapid, and requires only a small sample, which is sometimes an important consideration.

Calcium

Although the turbidimetric determination of calcium after precipitation with ammonium oxalate in neutral solution was reported by Hinds[5] to give accurate results, the method has not been found generally applicable to natural waters. A number of experiments were made with oxalic acid and potassium oxalate to find the proportions which would give the most accurate turbidimetric determination of calcium, but the best proportions of these reagents did not give results of the accuracy of the turbidimetric determination of sulfate. When acetic acid was substituted for oxalic acid much better results were obtained. The results of a large number of tests with different quantities of the reagents led to the selection of the details of the method given below.

Samples of 10 cc. of the water to be tested are taken in test tubes and standards are prepared in other tubes containing in 10 cc. from 0.04 to 0.24 milligram of calcium. To each tube 1 cc. of acetic acid (equal volumes of 99.5 per cent acid and water) is added and the contents are well shaken. After the addition of 1 cc. of potassium oxalate solution (containing 0.2 gram $K_2C_2O_4$) the tubes are again shaken. The turbidities are compared after 10 minutes. The relative turbidities are quite constant for 3 or 4 hours, so it is not necessary to make the comparison at once. The upper limit for the determination of calcium as described is about 24 parts per million. Samples of less than 10 cc. are taken for the more concentrated waters, as is done for sulfate, and the volumes made to 10 cc. before the addition of reagents.

The differences between the analytical results and the turbidimetric results for calcium in one hundred seventy-four samples of water are shown in Fig. 2. The differences and the analytical results are divided by the appropriate factors for the samples of which less than 10 cc. were used for the turbidimetric determination. It is evident that the accuracy is about the same as for the determination of sulfate. The average percentage error is 19 per cent of the analytical result. The error of 28 per cent for the sixty-eight samples of 10 cc. corresponds to an average error of 2.2 parts per million of calcium, which is not generally of any significance.

The results shown in Fig. 2 make it plain that the turbidimetric method described is sufficiently accurate for a preliminary determination, but cannot be depended upon to give results that can be used with the same confidence as the results obtained by the ordinary analytical methods.

Hardness

The soap method for hardness, practically as originally devised by Clark,[6] is recognized in all texts as useful for approximate determinations. Some of the criticisms of the method have been based on results obtained with details of manipulation different from those generally recommended, and therefore do not apply to the method as now used.

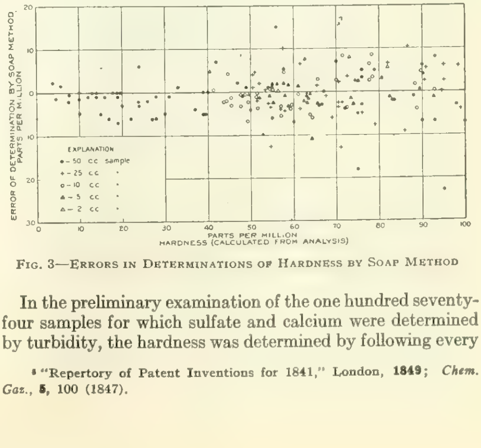

Fig. 3—Errors in Determinations of Hardness by Soap Method

In the preliminary examination of the one hundred seventy-four samples for which sulfate and calcium were determined by turbidity, the hardness was determined by following every detail of the soap method as given in Standard Methods of Water Analysis of the American Public Health Association. If the hardness of a sample was over 100 parts per million, less than 50 cc. were taken for the test and the volume made up to 50 cc. with distilled water.

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[6] "Repertory of Patent Inventions for 1841," London, **1849**; *Chem. Gaz.*, **5**, 100 (1847).

The hardness of each water was calculated from the calcium and magnesium determined in the regular analysis. The difference between the determined and calculated hardness for each sample is plotted against the calculated hardness in Fig. 3. The errors for determinations above 100 parts per million have been divided by a factor corresponding to the quantity of water used in the soap test, as was done with the sulfate and calcium results.

It is evident that the soap method for hardness is more reliable than the rough turbidimetric methods for sulfate and for calcium. The average percentage or difference between the calculated and determined hardness for the one hundred seventy-four samples is 8 per cent of the calculated hardness.

The Titration of Hydrofluoric and Hydrofluosilicic Acids in Mixtures Containing Small Amounts of Hydrofluosilicic Acid[1]

By **Paul H. M.-P. Brinton, Landon A. Sarver, and Arthur E. Stoppel**

University of Minnesota, Minneapolis, Minn.

THE determination of hydrofluoric and hydrofluosilicic acids in mixtures of the two has been investigated by a number of workers,[2] and the problem is of considerable importance because it is really encountered in every analysis of the hydrofluoric acid of commerce. A study of the method given by Scott[3] forms the subject of this paper.

In this method the sample of the mixed acids, to which has been added some potassium nitrate, is first titrated ice cold with standard sodium hydroxide, using phenolphthalein as indicator; and then the titrated solution is heated to about 80° C., and again titrated to a pink end point. The reactions for these two titrations are as follows:

For the cold end point:

$$H_2F_2 + 2NaOH \longrightarrow 2NaF + 2H_2O$$
$$H_2SiF_6 + 2KNO_3 + 2NaOH \longrightarrow K_2SiF_6 + 2NaNO_3 + 2H_2O$$

For the hot end point:

$$K_2SiF_6 + 4NaOH \longrightarrow 4NaF + 2KF + Si(OH)_4$$

From the equations the results of the titrations for the two acids are readily calculated.

Results of analyses of the same sample made in three different laboratories by this method showed wide divergence. Not only were the final results at variance, but there was considerable difference in the ease with which the end points, particularly in the cold titrations, could be detected. Investigation of the causes of these differences has led to the uncovering of sources of error which the writers believe are responsible for the dissatisfaction with the method which has been expressed in some quarters.

Weighing of Sample

It is customary in many laboratories to transfer the sample from the bottle to a platinum weighing vessel by means of a lead thief or lead pipet. The writers noticed in some of their early experiments that the tip of the lead tube became corroded, and found that if the tip of the pipet were allowed to touch the platinum as the acid was flowing from the tip, a brisk evolution of gas occurred and the lead was rapidly attacked as a result of the galvanic couple. If the lead is not allowed to touch the platinum there is no action.

With small platinum weighing vessels, even if opened under alkali, there is apt to be loss of hydrogen fluoride vapors when the vessel is first opened. This source of error has been corrected by weighing the sample in a rubber bottle[4] which has been nearly filled with cracked ice and then weighed. To overcome the change of weight due to condensation of moisture on the cold bottle during weighing, the bottle is weighed in a stoppered weighing bottle, well lined with asbestos paper, and counterpoised by a weighing bottle of similar external form on the opposite balance pan. After weighing, the bottle is shaken once or twice to absorb any vapors of hydrogen fluoride, and the sample, then in the form of an ice-cold, dilute solution, can be poured and rinsed into the alkali without loss.

End Point and Indicator

Methyl orange cannot be used because of the weak nature of the second hydrogen of H_2F_2. This leads to the formation of acid salts as intermediate reaction products, which have the strength of weak organic acids. Phenolphthalein, however, is satisfactory. Scott[3] suggests as the end point for the cold titration a pink that will persist for 15 seconds. It is self-evident that an alkali solution free from carbonate must be used, for even at this temperature the end point with phenolphthalein when using a solution contaminated with carbonate is not only misplaced, but is also faint and fleeting. If the solution is not icecold for the first end point, the color will rapidly fade due to hydrolysis of potassium fluosilicate. Katz[5] has suggested that this hydrolysis proceeds much more rapidly in the presence of calcium salts, owing to disturbance of equilibrium due to formation of insoluble calcium fluoride, and it was thought that perhaps calcium oxide would be inadmissible as a reagent for removing carbonate from the standard alkali; but the amount of calcium oxide which can exist in a sodium hydroxide solution is found to have a negligible effect.

Effect of Silica in the Standard Alkali

Apparently, the most serious source of error in the use of this method is the silica content of ordinary alkali solutions. In tracing out the cause of the divergence in the analytical results obtained in three laboratories on the same sample, it was found that one alkali solution was freshly made, one was several months old, and one was two years old. The carbonate had been recently removed from all the solutions by calcium oxide. The percentages of hydrofluosilicic acid reported by the three laboratories were 1.54, 2.24, and 5.52, in the order of the ages of the sodium hydroxide solutions. A determination of the silica in these standard alkali solutions showed that they contained 0.02, 0.07, and 0.32 gram of silica per liter, in the order of their ages. Tests with standard alkali solutions intentionally contaminated with silica, by the addition of varying amounts of water glass, showed that the presence of this silica exerted a tremendous effect in lowering the apparent percentages of hydrofluoric acid and increasing that of hydrofluosilicic acid.

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[1] Presented before the Division of Inorganic and Physical Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Guyot, *Compt. rend.*, **71**, 224 (1870); Katz, *Chem. Ztg.*, **28**, 356, 387 (1904); Greef, *Ber.*, **46**, 251 (1913); Dinwiddie, *Am. J. Sci.*, **192**, 421 (1916); Huddleston and Bassett, *J. Chem. Soc.* (*London*), **119**, 403T (1921).

[3] "Standard Methods of Chemical Analysis," **1922**, p. 1019, D. Van Nostrand Co.

[4] Hard rubber bottles of 0.5-ounce capacity have been found very satisfactory for this purpose.

[5] *Chem. Ztg.*, **28**, 356 (1904).

Lots of sodium hydroxide made from sodium metal by the action of water vapor, the sodium hydroxide being caught in platinum and stored in bottles lined with ceresin, were used by the analysts in the different laboratories, and the former discrepancies disappeared. The rapidly fading "cold end points" of the earlier analyses were no longer in evidence, and sharp end points in which the pink persisted, not for 15 seconds, but for from 1 to 4 minutes, were easily obtained.

Electrometric titration curves obtained in a hydrogen electrode apparatus, all the glass parts of which were heavily paraffined, showed that in the absence of silica in the standard alkali solution the hydrolysis of the potassium fluosilicate in ice-cold solution was sufficiently slow to allow a ready reading of the cold end point, whereas in the presence of appreciable amounts of silica in the alkali, the change in the hydrogen-ion concentration on standing was much more rapid, and the end-point color correspondingly fleeting.

In order to determine quantitatively the exact effect of silica on the analyses, a series of standard alkali solutions of varying silica content were made from sodium metal, with subsequent additions of pure sodium silicate which had been obtained by acidifying sodium silicate solution with hydrochloric acid, boiling off carbon dioxide, mixing with pure sodium hydroxide solution, warming, and filtering. The silica content of these standard alkali solutions was accurately determined gravimetrically.

TABLE I—RELATION OF ANALYTICAL RESULTS TO AMOUNTS OF SILICA IN STANDARD ALKALI SOLUTIONS

Grams SiO_2 per Liter NaOH	Per cent HF Found	Per cent H_2SiF_6 Found
0.036	51.01	2.36
0.180	49.78	4.05
0.252	48.84	4.90
0.396	47.10	6.58
0.536	45.89	8.12

The importance of the effect of silica will be understood when it is realized how rapidly silica is taken up from a glass bottle by a sodium hydroxide solution. As an example, a standard alkali solution freshly prepared showed 0.020 gram of silica per liter. After standing less than four months this solution showed 0.092 gram of silica per liter, which would make a percentage error of nearly 40 per cent in the amount of hydrofluosilicic acid reported in that particular sample.

It will be seen from Table II that the silica in the standard alkali added to the solution up to the cold end point is all converted to hydrofluosilicic acid, and is so registered in the analysis—that is, the silicon tetrafluoride first formed by the action of the hydrofluoric acid on the silica is completely hydrolyzed to fluosilicic acid. Naturally, any silica in the alkali added after the cold end point has been passed would not count, because there would be no free hydrofluoric acid left to react with it. In Table II all samples are calculated to a 1-gram basis for ease of comparison.

The column $c-b$ in Table II, when multiplied by 100, gives the percentages of hydrofluosilicic found in the analyses after deducting the amount of hydrofluosilicic acid equivalent to the silica added in the form of impurity in the standard alkali. These percentages run from 1.92 to 2.04, which for this determination may be considered a satisfactory degree of concordance. The gradual increase in the percentage of (corrected) hydrofluosilicic acid found with increasing amounts of silica introduced as impurity cannot be definitely explained at this time, but it is doubtless connected with the increasing difficulty of detecting the cold end point as the amount of silica increases. It should be noted, however, that with the lower amounts of silica, such as would be found in solutions of reasonable freshness, the deviation is very slight, and it is well within the limit of accuracy of the method.

TABLE II

(a) SiO_2 Added G.	(b) H_2SiF_6 Equivalent to SiO_2 Added G.	(c) H_2SiF_6 Found G.	(c − b) Corrected H_2SiF_6 G.
0.00182	0.00436	0.0236	0.0192
0.00883	0.02113	0.0405	0.0194
0.01227	0.02936	0.0490	0.0196
0.01898	0.04543	0.0658	0.0204
0.02542	0.06082	0.0812	0.0204

CONCLUSION

In conclusion, if accurate results are desired by this method, it is suggested that a determination of silica be made in even freshly prepared solutions of standard alkali, and that corrections be applied to the figures found for the two acids. One molecule of silica will react with six molecules of hydrofluoric acid to form one molecule of hydrofluosilicic acid. Therefore, the weight of silica added during the titration up to the cold end point should be multiplied by the factor H_2SiF_6/SiO_2, or 2.393, to find the weight of hydrofluosilicic acid to be deducted from the weight of hydrofluosilicic acid found; and by the factor $6HF/SiO_2$, or 1.991, to find the weight of hydrofluoric acid to be added to the weight of hydrofluoric acid found.

Explosion at Bureau of Standards

On the afternoon of September 20, a violent explosion followed by fire occurred in the dynamometer laboratory of the Bureau of Standards. One man was killed instantly, three others were injured so seriously that they died during the night, and four others seriously burned or cut. The heroism of the survivors of the staff in rescuing the injured from the furiously burning wreckage and in shutting off the electric circuits and the ammonia valves, minimized the loss of life and property.

The explosion occurred in the altitude chamber which is used in testing the performance of aircraft engines under the conditions of low pressure and temperature obtaining at high altitudes. At the time of the accident the room was being used in investigating the performance of an automobile engine, at temperatures corresponding to winter operation, using various grades of gasoline. The work was intended to determine the possible increase in gasoline production per barrel of crude oil, with the accompanying conservation of our natural resources, by the use of gasoline of lower volatility.

The explosion was due to the ignition of an explosive mixture in the chamber.

The dead are:	The injured are:
Logan L. Lauer	Henry K. Cummings
Urban J. Cook	Frank E. Richardson
Stephen N. Lee	Roger Birdsell
Joseph Kendig	George W. Elliott
	C. N. Smith
	R. F. Kohr

Most of these men were college graduates with experience and skill in research work, and a grave blow to science and engineering must be added to the human loss to their families and colleagues.

Thus grows the long list of those who have given their lives for the increase of human knowledge and welfare.

The Fourth International Congress of Chemistry

Abstract of the Minutes of the Cambridge Meeting

By **Jean Gérard**, General Secretary

THE Fourth International Congress of Chemistry was held in Cambridge, June 17 to 20, 1923. Sir William Pope, president of the Union of Pure and Applied Chemistry and professor of chemistry of the University of Cambridge, presided. The program included meetings of the council, a meeting of the general assembly, and committee meetings.

The council met the day after an extremely cordial reception by the British Federal Council for Pure and Applied Chemistry, in the Arts School, to take up the question of new admissions and to lay out the program of the general assembly.

The admission of Brazil, whose government had applied for membership in the Union, was unanimously carried. The president of the conference brought out the point that the International Research Council does not allow its subsidiary international unions to accept new member-countries without these countries being first admitted to the International Research Council. The countries who desire to be admitted to the Union must therefore send a request for admission to the International Research Council and mention therein their desire to be admitted to the International Union of Pure and Applied Chemistry.

The general assembly at its subsequent meeting approved the report of the president on the acts of the council as well as the report of the auditor on the accounts for the fiscal year just closed, and approved the budget for the present year.

The second part of the meeting was devoted to the assignment of work among the different committees. These committees, after having duly met, submitted for the approval of the council, resolutions, of which a resumé follows.

I. The Committee for the Reform of the Nomenclature of Inorganic Chemistry proposed that the work in the future be placed in the hands of the editors of the principal journals, and especially those of the *Journal of the Chemical Society, Chemical Abstracts, Gazzetta chimica italiana, Helvetica Chimica Acta, Recueil des travaux chimiques des Pays-Bas*, and the *Bulletin de la société chimique de France.*

Each country is to send its suggestions to these various publications, which will be duly qualified to submit them for general discussion. It is the opinion of the committee that when nearly unanimous agreement has been reached methods could be devised to insure the adoption of the conclusions so that these could serve as a basis for new proposals.

The committee deems it necessary that reports, even if not complete, be sent to the central organ as soon as possible.

The decisions enumerated below must therefore be considered purely provisional:

1—Regarding the unification of chemical symbols proposed for Formula Index, the committee has not deemed it wise to insist immediately on its own authority on the acceptance of definite symbols for glucinium (Gl), beryllium (Be), niobium (Nb), or columbium (Cb). The committee feels, however, that next year a final decision must be reached, after due consultation of the nations represented. There are two points to be considered—the original names and the original symbols. Other points may be brought up for consideration. The decision on these questions, which must be reached before January of next year, will be communicated to the delegates who will sit at the next session.

2—The committee feels that the writing of formulas of acids, bases, and salts in each country should conform to the usual custom in any particular language—that is, in the countries of Anglo-Saxon languages one would write HCl, H_2SO_4, $BaCl_2$, Na_2SO_4, $Ba(OH)_2$, etc., whereas in the countries of Latin languages one would write ClH, SO^4H^2, SO^4Na^2, $BaCl^2$, $(OH)^2Ba$, but in the same language one should not write sometimes $ClNa$ and sometimes $NaCl$, nor sometimes SO^4Na^2 and sometimes Na_2SO_4.

3—The word "hydrate" will be reserved for combinations containing H_2O—like the hydrate of chlorine, $Cl_2.rH_2O$; the hydrate of sodium sulfate, Na_2SO_4, $10H_2O$. The word "hydroxide" will be reserved for chemical combinations containing OH—aluminium hydroxide, $Al(HO)_3$; barium hydroxide, $Ba(OH)_2$.

4—The committee accepts the names of acids as given in the French report when these agree with those in the Danish and American reports.

To the accepted list may be added chromic acid, H_2CrO_4; molybdic acid, H_2MoO_4; manganic acid, H_2MnO_4; and permanganic acid, $HMnO_4$.

Those parts of the report which do not agree will form the subject of subsequent discussion—for example, hyposulfite (hydrosulfite in French), pyrosulfuric acid, heptamolybdic acids, etc.

Condensed acids, like pyrosulfuric, heptamolybdic, etc., will be fully discussed later, but the committee feels that the suggestion submitted in the Spanish report to designate such acids by the prefix "anhydro," preceded by a numerical index and followed by the specific name of the acid with a numerical prefix, could be adopted as a basis for discussion—for example, chromic acid, H_2CrO_4, *di*anhydro-*tri*chromate $K_2Cr_3O_{10}$; iodic acid, HIO_3; *di*anhydro-*tetra*iodate, $M_2I_4O_{11}$, etc.

It might be possible for certain acids which stand out above the others on account of the large number of their derivatives, to preserve their names—as, for example, heptamolybdic acid, which applies exclusively to the hexacid $H_6Mo_7O_{24}$.

5—The acid salts will be named in accordance with the French report—for example, $CaHPO_4$, calcium acid phosphate; KH_2PO_4, dihydrogen potassium phosphate.

6—The degree of valence of metals in spoken language would be expressed as given by the French report without inconvenience for any country. This would end all the discussion on the terminations *-ous, -ic, -a, -o,* etc., which have been proposed various times.

7—The nomenclature of complex compounds on which a report has already been laid before the second congress ought to be taken up.

II. The Committee for the Reform of Nomenclature in Organic Chemistry presented the following resolutions:

1—The committee, organized at the Lyons congress and consisting of the editors of the *Journal of the Chemical Society, Chemical Abstracts*, and *Bulletin de la société chimique de France*, will be increased to six members by adding to it the editors of the *Gazetta chimica italiana, Helvetica Chimica Acta*, and of *Recueil des travaux chimiques des Pays-Bas.* These publications may designate a representative.

2—The question of nomenclature under discussion will be submitted to this committee of six. The suggestions emanating from individuals or national committees or committees of chemical societies, will be submitted to this committee.

The decisions of the Committee of Six must be unanimous. They will be submitted for approval at a meeting of the Union.

3—The Geneva nomenclature will be taken as basis for new discussions, and this resolution will be transmitted to the Committee of Six.

4—The Committee of Six may hold a special meeting for the purpose of exchanging opinions and facilitating subsequent work.

III. The Committee on the Reform of the Nomenclature of Biological Chemistry adopted the following resolutions dealing with the most general names:

1—The name of a new compound, the chemical constituent of which is known, must be made up in accordance with rules of nomenclature of organic chemistry.

2—The word "glucid" will be used to designate the group of substances which comprises the simple reducing sugars and substances which give one or several of these sugars by hydrolysis.

3—The word "lipoid" will no longer be used.

4—The word "lipide" will designate the group of substances which comprises the fat bodies and esters which possess analogous properties (lecithines, phosphatines, etc.).

5—The word "protide" will designate the group of substances which comprises the natural amino acids and substances which by hydrolysis give one or more of these acids.

IV. The Committee on Bibliography passed the following resolutions:

1—That the secretary of the Union make an investigation of the bureaus of documentation existing at the present time and publish a list of these bureaus with their addresses, their specialties, and a short description of their organization.

2—That the bureaus of documentation unify as much as possible their methods of work in accordance with the principles adopted by the International Institute of Bibliography and the Subcommittee on Bibliography of the League of Nations.

3—That the Union finance the printing of classification tables, standardized in their present form and provisionally revised, in order that these tables can be submitted to the critical review of competent experts in various countries.

4—That each country make a list of the journals directly interested in pure and applied chemistry and that these lists be brought together and distributed by the general secretary of the Union.

5—That, in view of the resolution of the Subcommittee on Bibliography of the League of Nations, chemical publications send at least two copies, and preferably five copies, of their annual index to the International Institute of Bibliography in order that this institute may be in a position to draw up the Central Annual Bibliographical Index of Authors' Names.

6—That the general secretary of the Union make every possible effort to persuade those publications which have not yet come to a decision to conform with the two following resolutions which were passed at the previous Congress:

(1) That all original papers in chemistry have the address of the author or that of the laboratory where the work was carried out.

(2) That the journals give a resumé of their articles in one of the languages accepted by the editorial board of the Annual Tables of Constants, in such a form that it could be published in an abstract journal.

V. The Committee on Physico-Chemical Standards passed the following resolutions:

1—That the committee approves the financial report of the Bureau of Physico-Chemical Standards for the fiscal year 1922–1923.

2—That it is the desire of the committee that the Bureau of Physico-Chemical Standards investigate, through circular letters addressed to the directors of the research laboratories, what are the new physico-chemical standards, the preparation of which would be most urgent. The results of such an investigation will facilitate coördinating the work of the bureau.

3—That in the opinion of the committee it will be well to ask the Bureau of Physico-Chemical Standards to study the possibilities of obtaining the coöperation of certain chemical firms specializing in the manufacture of pure products, and to submit to the next congress a plan to obtain such a coöperation.

4—That the committee congratulates Mr. Timmermans, secretary of the Bureau of Physico-Chemical Standards, on the fruitful and extensive work that he has carried out with remarkable devotion. The committee hopes that he may continue the publication of the critical tables of physico-chemical constants of organic compounds, this work being considered by the committee of an importance which could not be exaggerated.

5—That the committee would like to see a closer coöperation between the Bureau of Physico-Chemical Standards and the Committee on Pure Products for Research.

6—That the committee recommend to the council for the fiscal year 1923–1924 a supplementary appropriation of 15,000 francs.

VI. The Committee on Pure Products for Research, in answer to the question asked by the International Oceanographic Association of the Mediterranean, replies that pure sodium chloride may replace standard sea water for the volumetric determinations actually in use in oceanographic work.

In addition the committee passed the following resolutions:

1—That the list of pure products for analytical work be not made up until after the various countries represented on the committee have an opportunity to discuss the matter with their analytical chemists. Nevertheless, in order to avoid too long a delay in the carrying out of the work of the committee, the list of reagents enumerated in the index (Types of the Congress of 1922) will be temporarily adopted, this list being subject to further revision.

2—That the committee instruct its members to organize during the months following the meeting, and to distribute among the various members of the committee, or among the various competent persons designated by the committee, the experimental work necessary to complete the international list of pure products for analytical work.

3—That it is the desire of the committee that its president put himself in contact with the members of the Bureau of Physico-Chemical Standards with a view to finding a means to prevent the same reagent from being classified in one case as a pure product for analysis and in another case as a physico-chemical standard.

VII. The Committee on the Bibliography of Industrial and Technological Products desires that the bibliographical work on raw materials and industrial products, such as has been begun by the central office, be pushed along as actively as possible in every state represented in the Union, even though the number of manufacturers coöperating be small.

The committee requests that the Bureau of Vegetable Raw Materials, which is actually working in France, be incorporated in the Bibliographic Bureau of Industrial and Technological Products. The above-mentioned bureau is directed and subsidized by the French Parliament as well as by interested manufacturers. Its object is to complete the official work of the university in bringing together all information on the origin and quality of French and foreign drugs known in the market.

The committee requests that the Musée de la Faculté de Pharmacie de Paris and the Laboratoire Central d'Etudes et d'Analyses des Produits Médicamenteux et Hygiéniques (Laboratoire de la Commission du Codex) be incorporated in the central office. With the help of these three organizations it will be possible to bring together the bibliography concerning vegetable raw materials utilized in chemical industry in the manufacture of drugs and perfumery. The name of these united bureaus shall be "Service de Documentation sur les Matières Premières et les Produits Industriels" (Bureau of Bibliography of Raw Materials and Industrial Products).

VIII. The Committee on the Choice of a Thermochemical Standard took note of the decision reached by the Bureau of Standards, Washington, that the benzoic acid prepared by this bureau cannot be obtained as standard substance for calorimetric determinations except for purely scientific purposes, and that it becomes therefore necessary to employ for technical purposes, in the determination of heats of combustion of solid and liquid fuels, benzoic acid from other sources.

The committee recommends, nevertheless, that the standardizing of calorimetric bombs be carried out by the use of samples of benzoic acid which have been duly approved by a competent thermochemist. The committee will eventually take up the question of drawing up necessary instructions for the approval of such samples.

The committee deems it necessary that, in converting thermochemical data determined in calories into absolute units, and vice versa, use should be made of the conversion factor: 1 calorie 15° C. = 1184 joules, the average value accepted at the present time, in accordance with the decisions reached in 1923 by the International Critical Tables, following the advice of several scientific societies.

IX. The Committee on the Tables of Constants unanimously passed the following resolutions:

1—That the Union approve the financial report submitted by the Committee on the Annual Tables of International Constants of Chemistry, Physics, and Technology for the fiscal year 1922, and that this report be transmitted to the International Research Council.

2—That the attention of the Union be called to the fact that the following countries have contributed to the International Fund created in 1922: Belgium, Denmark, Spain, the United States, Great Britain, France, Italy, Norway, the Netherlands, Portugal, Switzerland, and Czecho-Slovakia.

Concerning those countries which do not appear on the above list but whose contribution may be considered as practically certain the Union should pass a resolution to the effect that this should be made with the least possible delay.

3—That the Union should take cognizance of the final organization of the International Fund, the necessity for which had been recognized in Lyons in 1922, and signify its appreciation of the value of the annual international tables as a bibliographic publication indispensable to scientific and technical progress.

4—That the Union should pass a resolution recommending that the numerical bibliography of the years 1917–1922 be published as rapidly as possible in order that the International Tables of Constants and Numerical Data resume as soon as possible its annual publication.

The committee hopes that it will be possible for the committee on the tables to carry out its plans with the help of the annual subscription open for that purpose under the patronage of scientific and industrial societies of the adhering countries.

Regarding physico-chemical symbols, the committee includes the following modifications:

1—The second part of the list of symbols should have for its title "General Constants" instead of "Universal Constants."

2—In the third part, ninth line, "molar fraction" should be substituted for "mol fraction."

3—Page 305, fifth part, second line, the symbol n in the column "Alternative Symbols" should be omitted.

4—Fifth part, eighth line, replace $M(\alpha)$ by M as a symbol for molecular rotatory power.

5—Fifth part, last line, replace $M(\omega)$ by (Ω) as a symbol for molecular rotation.

6—Page 506, third line from bottom of page, suppress the words "Soschmidts Numbers."

7—Page 509, in paragraph headed "Entropy," second line, suppress the words "on the ground that this symbol was used by Willard Gibbs, and also***"

8—Page 511, in accordance with general custom the molecular rotation is defined by the relation

$$M = \frac{M \times (\alpha)}{100}$$

The employment of ω for the specific magnetic rotation and Ω for molecular magnetic rotation is recommended; the molecular magnetic rotation is defined by the relation

$$\Omega = \frac{M \times (\omega)}{15}$$

In the alphabetical list these changes should be taken into account.

The committee proposes to appoint a subcommittee for the purpose of bringing together the suggestions leading to additions or changes in the list of symbols and to put forth proposals. This committee will be headed by Professor Cohen and will include Messrs. Findley, Marie, and an American member to be appointed by the National Research Council of the United States.

X. The Committee on Solid Fuels decided to complete the work undertaken in the countries adhering to the Union on the nomenclature of solid fuels, as well as on the methods of determining their essential characteristics, especially the volatile content, the calorific power, and the agglutinating power. The committee insists that the answers should reach the general secretary before January, 1925.

XI. The Committee on Liquid Fuels decided to extend the work undertaken on the nomenclature of different groups of liquid fuels as follows: petroleum and its derivatives; distillation products of coal, lignite, peat, wood and bituminous shales; alcohol; vegetable oils.

The committee requests that answers reach the general secretary before January 1, 1925.

XII. The Committee on the Study of Ceramic Products passed the following resolutions:

1—That the Union recommend that from a technical and scientific point of view the term "ceramic" be employed for all industries manufacturing the following products:

(*a*) All kinds of burned clay products, such as stoneware, earthenware, brick, tile, sewer pipe, terra cotta, china, porcelain, etc.

(*b*) Cementing materials, such as portland cement and dental cement; lime, plaster, and a variety of magnesia and gypsum products whose constituents are of an earthy nature and which, after a preliminary treatment which involves a calcination, acquire the property of "setting" to a greater or less extent, when mixed with the proper liquids.

(*c*) All varieties of glass and glassware, including quartz glass, glazes, enamels, and many of the artificial precious stones.

(*d*) Enameled metal products, where the enamel itself is a ceramic material applied to the metal at high temperature, the metal serving only as a skeleton to give the desired form and strength to the glass which it supports.

(*e*) Refractory articles or materials, either wholly or partially composed of or manufactured from clay, silica (in its various forms), alumina (bauxite), magnesia (magnesite), lime, chromite, asbestos, zirconia, mica, the rare earths, certain carbides and nitrides, and in general any nonmetallic product capable of withstanding elevated temperatures. In all products of this class it is evident that a high temperature treatment is fundamental.

(*f*) Abrasive materials such as carborundum, alundum, and zirconia (and by association, finely divided silica and emery), together with the products manufactured from them by bonding with an earthy material.

(*g*) Various electrical and thermal insulating products in the manufacture of which earthy materials enter as an important element.

2—The committee recommends that in each country an exact nomenclature of raw materials and manufactured products of the ceramic industry be instituted together with their chief characteristics.

3—The committee proposes unanimously that the question of the choice of standards of various earths to be used in the study of chemical and physical properties of refractory materials, as well as the proposed methods of studying such properties, be included in the program of the next congress.

4—On the proposal of M. Henry LeChatelier and M. Capsa, members of the committee, the committee believes that the proposed work ought to be done by various laboratories in all countries, and it hopes that this work will be carried out with the same raw materials in order to reach comparable conclusions.

It is the opinion of the committee that it will be desirable to agree on the form of apparatus to be employed for the determination of dilatation coefficients.

5—The committee hopes that M. Henry LeChatelier will be willing to undertake the direction of the necessary researches and look after their proper coördination.

XIII. The Committee on Food Preservation passed the following resolutions:

1—That as soon as possible the various countries belonging to the Union, who have not yet appointed a delegate, do so in order that the membership of the committee be completed.

2—That the subcommittee of five members composed of Messrs. Alsberg, Bordas, Paterno, Pondal, Voerman, present at the next congress a general report on the bibliography which has been gathered up to the present, and which could be assembled from now until then, in regard to all matters relating to food legislation in the various countries.

3—That at the time of the next congress the delegates of the various countries, taking into consideration the legislation in force at the time, present their conclusions as to the effects of employing the following products as food preservatives: benzoic acid, boric acid, salicylic acid, sulfurous acid, sulfates and formaldehyde, for the purpose of undertaking a systematical and physiological investigation on the possibility of using chemical products in food preservation.

4—That the chemists of all nations submit opinions concerning the chemical processes of food preservation, in order that steps tending towards uniform legislation founded on experimental basis be initiated.

5—That the coöperation of the "Laboratoire International d'Analyse des Matières Destinées à l'Alimentation des Hommes et des Animaux" be requested for the researches to be undertaken.

XIV. The Committee on Scientific and Industrial Ownership presented the following resolutions:

1—The committee, considering that in the Latin group, which is composed of countries granting patents without examination, the unification of legislation appears to be more capable of realization than in the others, invites these countries to get together as soon as possible with the idea of forming the first group with uniform legislation.

2—Considering that the original purpose toward which one must work should be to permit research workers to protect their discoveries, and considering that on the other hand research workers cannot carry out their researches in secret, but must on the contrary, be able to publish the results of their work as they are obtained, the committee resolved:

> That it is inadmissible that one should oppose to the holder or the applicant of a patent the results of his own work for a certain period of time after it has been published.

3—The committee declares that a purely scientific discovery should be legally protected.

4—A proper definition of this new legal right will be studied by the committee.

5—In order to secure the coördination of all efforts the president of the committee is appointed as a delegate to the Committee on Intellectual Coöperation of the League of Nations and to the International Chamber of Commerce to present and uphold the views of the committee.

XV. The Committee on Industrial Hygiene passed the following resolutions:

1—All the reports submitted on the question of dusts should be printed and distributed, as they contain matters of great interest which it would be most important to disseminate.

2—The committee requests the Council of the International Union to give a prize for the best published essay on smokes, gases, fogs, and noxious vapors to be met with in manufacturing, their elimination, and the protection against their effects. The essays submitted should be general and descriptive in character, should include the latest progress in their particular subject, and should be within the reach of the general reading public.

The council of the Union should undertake their distribution.

The committee requests that the council of the Union establish a prize to be given to the inventor of an apparatus of recent construction for the suppression of smoke. In case no recent inventor could be found the prize should be given to that person who had done the greatest amount of work and obtained the best results on the problem of the suppression of smoke.

The committee requests that the council communicate with all chemists specializing in this particular branch in order to obtain from them their scientific results on this matter, and that they also furnish exact data on (*a*) the noxious effects produced on the workmen and the neighboring communities by certain emanations, and (*b*) the means employed to suppress them.

3—The committee requests that each nation send to the next congress a complete report on the legislation concerning industrial hygiene in its own territory. This report should include the legal matters covering differences of work and those covering the suppression of nuisances to neighboring communities. Each country should communicate to the general secretary a list of the administrative organizations charged with the drafting and enforcement of laws and regulations concerning industrial hygiene.

4—The committee requests that its president collect information on the following subjects:

(*a*) Methods of analysis employed in the determination of the quantity of hydrofluoric acid present in the smokes and vapors where it is likely to be found, especially in superphosphate manufacture.

(*b*) Determination of the minimum value of acidity in smokes when these have been discharged. This figure is fixed in Germany at 5 grams per cubic meter, in England at 8 grams per cubic meter, and in Italy at 6 grams per cubic meter, expressed in SO_2. The committee recommends that it would be wise to agree on a figure acceptable to all, and that it would be well to obtain agreement on the method of determination and on the method of expressing this figure.

(*c*) The possibility of suppressing offensive odors in industry when these are due to more or less unknown products which cannot be condensed, as, for example, in sewage disposal, slaughter houses, etc.

5—The committee requests that at the next congress a report be made on all methods and apparatus intended to combat incipient intoxication from poisonous gases in factories.

6—The bibliography and the resolutions of the committee should be communicated to the Bureau of Hygiene of the League of Nations and to the International Labor Bureau.

XVI. The Committee on Finance passed the following resolutions:

1—The committee, after having examined all the requests for appropriations made by the various committees, records that owing to the present state of the finances of the Union it cannot grant all the requests that have been made.

2—As a supplementary appropriation, after having studied the difficult financial situation faced by the Bureau of Physico-Chemical Standards, it decided to grant to this committee for the period extending from April, 1922, to November, 1924, the sum of 7500 francs, instead of 15,000 francs as requested.

The Committee on Finance finds itself restrained by the principle that the contributions from the countries belonging to the Union are essentially intended for the administrative expenses of the Union. The committee requests that the various committees should address themselves to the general secretary for all matters concerning correspondence and printing.

All these conclusions and resolutions were unanimously adopted by the council of the International Union at its meeting of June 20.

In order to expedite the work of the Union and to insure the continuity of it during the space intervening between the two meetings, the council requested the executive committee to ask the member of each permanent committee to appoint by correspondence a president to serve until 1925—that is, for the same period as the members of the present committees.

Following the decision to increase the number of vice presidents of the Union to six, the council nominated by acclamation two new vice presidents, E. Cohen (Netherlands) and Dr. Sakurai (Japan).

The council adjourned after having chosen Copenhagen as the place of meeting for the Fifth Congress of the International Union of Pure and Applied Chemistry.

All these decisions were placed before the delegations at the closing meeting of the general assembly.

The congress decided in closing to create a committee to coöperate with those organizations which undertake to exchange students and professors between the universities of the various countries with the idea of bringing about such exchanges among professors of chemistry

Meeting of Missouri Section

The Missouri Section of the AMERICAN CHEMICAL SOCIETY started its year's work on the evening of September 20. Dr. Philip A. Shaffer, professor of biological chemistry from the Medical School, Washington University, St. Louis, was the speaker of the evening. His topic was "Insulin, Its Properties and Methods of Preparation." Dr. Shaffer has done much toward the improvement of the methods of separation of this remarkable substance, and his talk on the disease diabetes and its relief by this substance was very enlightening to the many who were present. The meeting was the largest that has been held for some time; the fact that the audience was made up of people of widely scattered interests seemed an indication that there is a need that the local section can fill in bringing speakers here.

New Chemistry Building at Missouri

Following its plans for the expansion of the Chemistry Department, the University of Missouri is just completing a new building for the chemical work. This building is the third building on the campus to be devoted entirely to chemistry. There will be an auditorium seating 175 students, and laboratory locker space for 600 students. There are five small research laboratories for instructors, besides administration offices and storerooms. The attic has been finished off into four rooms and will probably be used as research laboratories for graduate students.

Denatured Alcohol Production

PRODUCED, USED, REMOVED, OR DUMPED, AS INDICATED BELOW, FOR THE

Formulas	Denatured Alcohol Produced					Removed from Denaturing Bonded Warehouses	Alcohol and Denaturants Dumped	
	1907	1908	1909	1910	1911	1912	1913	1914
				Completely Denatured Alcohol				
1							4,961,105.20	4,932,494.32
2							261,135.58	280,635.24
3								
4								
5								
9								
Total C. D. A.		1,812,122.38	2,370,839.70	3,076,924.55	3,374,019.92	4,229,741.67	5,222,240.78	5,213,129.56
				Specially Denatured Alcohol				
		Denatured Alcohol Used				Alcohol and Denaturants Dumped		
1		768,476.63	1,258,120.07			2,493,630.86	2,839,020.80	3,055,817.33
2		60,144.07	65,141.77			49,665.00	75,517.40	69,135.94
2-A		35,097.24	110,460.49			172,723.20	201,468.80	162,091.61
2-B								45,928.13
3		63,520.68	36,422.04			8,638.37	9,229.55	3,039.42
3-A							59,165.43	225,813.65
3-B								
4		288,981.36	365,590.06			403,943.91	511,329.65	564,010.34
4-A								
5		524.11	5,978.45			5,922.51	5,579.10	6,310.71
6		31,946.49	4,077.90					
6-A			16,730.77			194,869.32	229,014.73	245,755.56
6-B								
7		186.39						
8		190.19	1,069.95			742.40	989.70	804.40
9		3,930.48				3,992.96		
10			233.53					15,206.45
11		332.95	1,198.84			1,339.15	1,049.96	912.06
12		34,129.43	39,387.41			20,099.87		
12-A						5,344.70	15,456.31	11,122.47
13								
13-A		211,495.49	266,846.70			377,993.71	471,110.53	599,634.61
14		264.16	1,171.81			1,770.80	1,660.28	2,426.54
15		1,582.34	6,916.42			5,781.26	5,567.98	6,690.46
16		554.44	4,089.84			5,338.00	5,634.70	5,053.27
17			1,661.54			8,454.36	9,585.54	8,259.80
18						172,596.06	166,890.26	160,692.86
19						400.00	47.04	3,140.42
19-A								
20								
Total S. D. A.		1,501,356.45	2,185,097.59	3,002,102.55	3,507,109.94	3,933,246.44	4,608,417.76	5,191,846.03

TAX-FREE denatured alcohol was first produced in the United States under the Act of June 7, 1906, "for use in the arts and industries and for fuel, light, and power." Supplemental laws were later enacted, with the result that the manufacture and use of that product soon became a vital factor in the commercial life of the nation, and was recognized as a "key" industry during the World War.

The advent of prohibition presented an added, and perhaps more potent, reason why pure ethyl alcohol should be replaced as far as possible with tax-free denatured alcohol, and Section 10, Title 3, of the National Prohibition Act provided for denaturing plants at which ethyl alcohol could be lawfully denatured "by the admixture of such denaturing materials as shall render the alcohol or any compound in which it is authorized to be used unfit for use as an intoxicating beverage." To date, however, the Government has not extended the use of tax-free denatured alcohol to the production of pharmaceuticals or other commodities, intended for "internal" consumption, however unfit the final product may be for use as an intoxicating beverage. It is thought that this attitude with respect to "internal" medicines, etc., is more a question of administrative policy than law, and that eventually the Government will recede from its position in the interest of legitimate chemical development.

As indicating the progress of the denatured alcohol industry from humble beginnings to its present large proportions, we publish this table compiled by the office of James P. McGovern, the Washington attorney of the U. S. Industrial Alcohol Company. Although the columns for the years covered are variously headed, "Denatured Alcohol Produced," "Removed from Denaturing Bonded Warehouses," "Denatured Alcohol Used," "Withdrawn from Denaturing Plants," etc., as they appear in the Annual Reports of the Commissioner of Internal Revenue, the tabulation is to be regarded in its entirety as conveying a fairly comprehensive idea of the amounts, *by formulas*, of both completely and specially denatured alcohol *produced and used* during the fiscal years involved. It is regretted that it was not possible to have the compilation complete in all respects. The reason for the omissions will be found in the "Note," page 1087. The figures for the fiscal year ending June 30, 1923, are not yet available.

Space does not permit the listing of the innumerable uses for which denatured alcohol has been authorized. It is sufficient to say that specially denatured alcohol, Formula 1, alone has been prescribed for over two hundred and fifty items. Any one interested in such uses, however, may find the composition of the formulas and their respective uses fully set forth in the Appendix to Regulations No. 61 of the Internal Revenue Bureau, published September, 1922, under the title "Formulas for Completely and Specially Denatured Alcohol." Copies of such appendix may be had by addressing the Industrial Alcohol and Chemical Division, Internal Revenue Bureau, Washington, D. C.

In studying the table it should be noted that more than half of the formulas have come into existence since the World War, and most of these since prohibition. While the total amounts for each of the fiscal years ending June 30, 1916, 1917, 1918, and 1919, respectively, exceed those for 1920, 1921, and 1922, the difference may be largely attributed to the tremendous withdrawals of Specially Denatured Alcohol, Formula 2-B, for the manufacture of smokeless powder, trinitrotoluene and other war materials, and a comparison of the totals of the years shown (excluding the war years) will reveal with greater accuracy the normal but rapid growth of this husky industrial infant.

Denatured Alcohol Production *(Concluded)*

FISCAL YEARS SHOWN, ENDING JUNE 30, RESPECTIVELY. (QUANTITIES IN WINE GALLONS)

Formulas	Alcohol Denatured under Various Formulas			Removed from Denaturing Bonded Warehouses			Withdrawn from Denaturing Plants	
	1915	1916	1917	1918	1919	1920	1921	1922
				Completely Denatured Alcohol				
1	5,149,410.88	7,184,620.75	9,140,999.26	8,313,416.96	7,180,520.30	6,926,825.22	50,420.00	166,215.87
2	237,236.08	687,332.07	1,367,920.08	1,974,904.37	2,806,520.76	2,451,144.07	251,201.30	300,191.79
3						28,323.97	50,042.82	117,370.94
4					1,433.11	390,558.01	268,315.34	22,595.75
5						3,679,944.90	6,496,719.23	9,843,651.33
6							5,109,820 18	5,759,877.15
Total C. D. A.	5,386,646.96	7,871,952.82	10,508.919.34	10,288,321.33	9,988,566.17	13,476,796.17	12,226,518.87	16,209,902.83
				Specially Denatured Alcohol				
1	3,026,030.54	4,504,202.02	4,685,613.19	4,228,493.16	4,402,655.07	6,563,351.12	3,993,825.77	4,994,240.74
2	80,547.02	421,849.00	176,655.65	214,055 88	88,553.44	112,518.66	64,722.63	
2-A	201,488.86	319,462.86	69,444.70	65,747.48	36,517.62	115,548.56	38,770.01	72,731.38
2-B	3,357,154.38	27,855,774.23	28,551,736.36	27,843,909.08	16,275,674.09	2,331,322.09	1,990,326.16	2,450,939.20
3	398.50	3,944.82	5,767.84				548.01	35.02
3-A	224,891.50	274,945.74	230,455.28	222,993.33	214,441.89	344,279.89	229,908.85	540,770.88
3-B	339 07	172.70	723.28	14,807.66	21,398.68	7,515.06	10,370.82	8,493.23
4	582,258.48	664,787.04	868,065.29	904,023.33	745,704.61	871,198.39	679,547.60	898,947.81
4-A								
5	5,617.41	7,228.91	6,581.46	5,532.29	7,277.08	41,463.68	5,763.75	8,193.93
6								3,272.64
6-A	238,961.22	456,091.25	318,679.45	444,355.77	804,780.71	86,850.35	99,318.44	67,107.65
6-B	525.53	409.00	5,039.00	5,739.92	11,793.75	13,671.67	5,829.06	8,084.42
7								
8	1,173.67	1,124.40	504.98		5,205.04	1,564.41		4.85
9	46.30	112.10	7,561.66	3,528.91	5,747.41	11,748.82	2,385.33	5.04
10	15,167.82	49,700.81	125,528.97	154,149.84	309,940.21	854,610.34	73,801.31	5,559.29
11	1,313.00	851.60	1,441.65	923.10	735.86	990.20	781.16	651.92
12					2,974.79	12,933.49		
12-A	24,301.90	53,992.66	97,706.05	88,004.66	83,316.84	153,324.61	141,877.53	281,093.04
13								5.00
13-A	606,891.20	888,915.92	981,284.73	1,042,072.48	1,009,774.31	1,309,239.99	966,048.04	1,780,771.06
14	2,917.11	2,613.48	4,378.02	6,363.93	695.05	1,894.25	1,226.77	1,636.50
15	7,089.57	6,103.43	12,652.19	9,768.17	31,774.63	104,476.45	14,510.96	8,220.81
16	5,528.67	9,235.51	23,361.92	25,902.30	28,789.39	24,810.34	3,705.93	9,156.90
17	13,087.09	95,164.40	25,759.96	28,052.79	65,109.64	57,436.82	49,132.69	13,598.38
18	199,723.84	240,912.30	233,462.12	473,869.35	950,941.33	1,160,120.01	725,816.56	1,036,893.33
19	4,369.13	104,426.82	24,086.84	27,410.61	26,875.13	54,281.85	42,392.80	42,537.95
19-A								
20		12,415.40		69,810.43	66,783.20	13,775.94	12,445.70	13,034.83
21		2,832,717.16	8,656,805.58	3,608,711.26	2,913,700.00	405,826.96	65,100.00	1.00
22			7,689.07	3,920.65	2,945.30	40,032.39	50,340.73	7,608.61
23			16,857.87	20,739.18	19,029.62	22,514.21	58,271.04	23,446.05
23-A							137,517.65	466,831.61
23-B							262.27	1,073.24
23-C							1,467.21	5,739.20
23-D								986.44
23-E								
23-F								
24			17,177.00	8,818.22		24.52	640.49	1,308.44
25			11,311.13	121,384 48	88,104.27	131,787.53	112,491.18	149,191.99
26			2,100.28	14,111.28	23,001.28	75,404.84	9,340.16	4,962.55
27			2,246.77	49,970.95	20,799.88	54,988.28	37,797.87	48,758.10
27-A						885.05	7,785.44	9,706.92
27-B								5,395.18
28					26,399.34	197,290.50	123,477.92	74,054.75
28-A								
29						18,161.12		24,677.07
30					426.67	19,533.33	10,896.83	15,873.61
31					750.78	2,933.21	427.52	92.43
31-A						33,625.90	33,816.70	49,651.87
31-B						243.00	16,573.14	22,366.93
31-C							100.32	45.26
32						14,078.34		11.00
33						2,085.53	2,360.63	4,171.55
33-A								3,621.06
34							4,658.40	9,204.84
35								8,768.44
35-A								99,360.55
36							447.41	197,996.68
37							24,052.87	330,416.20
37-A								
38							962.74	6,555.72
38-A							404 18	2,315.08
38 B								690.93
38-C								
38-D								1,039.64
38-E								467.14
39							38 656.42	175,189.30
39-A							50,057.95	1,330,091.32
39-B								1,425,542.59
39-C								
39-D								
40							26,357.33	321,975.38
41								1,061.57
42								1,975.71
43								214.99
44								9,282.56
45								1,549.24
46								5.00
47								
Experimental					1,017.03	497.55		
Total S. D. A.	8,599,821.81	38,807,153.56	45,170,678.29	39,707,170.49	28,293,615.94	15,268,839.25	9,967,320.28	17,089,263.54

NOTE: Compiled from the Annual Reports of the Commissioner of Internal Revenue. Amounts for 1907, amounts by formulas of *Completely* Denatured Alcohol for 1908, 1909, 1910, 1911, and 1912, and amounts by formulas of *Specially* Denatured Acohol for 1910 and 1911 are not given in such reports and are not available.

AMERICAN CONTEMPORARIES

Frank Austin Gooch

IF IT be true, as some claim, that the general atmosphere of Boston is one of cultured manners, no better illustration of the influence of such an atmosphere could be selected than the subject of this sketch. No one who has ever come in contact with Professor Gooch can fail to carry away the impression that he has met a man of peculiar charm of manner. Born in Watertown, Mass., of parents belonging to families connected with the early history of the country and representing the highest type of culture, his early life was spent in the vicinity of Boston. His father was a prominent lumber merchant in Cambridge, and at one time chief assessor of that town. His mother was a member of the Coolidge family.

Frank A Gooch

He entered Harvard at the age of sixteen and was graduated with the class of 1872.

His early inclination was toward medicine, but upon graduation, and until 1875, he carried on chemical and mineralogical studies at Harvard, and at the same time acted as assistant to Prof. Josiah P. Cooke, who was famous in his day as an experimental lecturer. Doubtless Professor Gooch's skill in manipulation and his clearness in description of chemical phenomena, so characteristic of his later work as a teacher, had their origin in this early training.

During the years 1875–6, spent mainly in Vienna, he continued his studies along mineralogical and crystallographic lines at the Imperial Museum, and his fund of reminiscences of that period goes to show that he had the most delightful association with the director and others in authority there. Upon his return he received the degree of Ph.D. from Harvard.

He often speaks of the two years which followed, when he held the position of private assistant to Dr. Wolcott Gibbs, as of special value to him, and frequently quotes a common expression of that renowned chemist, famous in inorganic and analytical research, to the effect that "there is practically nothing which cannot be accomplished by patience and caustic potash."

It was probably during this period that Dr. Gooch developed patience and skill and his love for analytical chemistry. To him chemical analysis has never been what many, profoundly ignorant of the subject, have considered it, blind following of directions, or "cook-book chemistry," a term which has been responsible for much neglect of this great fundamental branch of chemistry. Dr. Gooch's mind, stored with a wealth of observed chemical phenomena, finds the greatest joy in devising new analytical processes and in overcoming the difficulties which to many a chemist have seemed to make an analytical procedure useless.

For ten years following his apprenticeship with Dr. Gibbs, his work gave him ample scope for the perfection of his technic in his chosen field. Analytical work in connection with the United States Tenth Census, 1879–1881, the North Transcontinental Survey, 1881–1884, and the United States Geological Survey, 1884–1886, contributed much in the way of preparation for his work at Yale, which really began with the completion of the Kent Laboratory in 1887. It was during this period that he enjoyed from time to time association with Dr. Rafael Pumpelly, the renowned geologist and explorer, and he often turns with great pleasure to the recital of a variety of experiences connected with field and laboratory work.

It was also during these years that much important work was done, such as the analysis of the waters of Yellowstone Park and the invention of the perforated platinum crucible for filtration. The latter alone has made his name familiar wherever careful analytical work is attempted. Shortly after the first description of this almost indispensable analytical device appeared, a well-known chemist said in an address: "The Gooch crucible is to modern analytical chemistry what the needle gun is to modern warfare." This encomium was doubtless more adequate at the time it was uttered than it would be today, when the needle gun has been surpassed by many other inventions, while the crucible still holds its place among necessary equipment.

In selecting Dr Gooch for a position at Yale the authorities chose wisely and well, for he combines the good qualities of administrator, teacher, and director of research. During a period of over thirty years, for he did not take even a week off during term time, until his retirement in 1918, he was at his post.

No man could have a more loyal group of followers than those who have worked with Professor Gooch. His sympathy and liberality are such that a conference with him always resulted in helpful suggestions and in an adequate supply of material for work when special material was needed. A request for a gram generally resulted in a supply of ten grams. As for crude chemicals, they were an abomination to him, and his associates could hardly persuade him to order them for any kind of work. Despite this policy there was on hand at the end of his administration a considerable balance in money to the laboratory's credit, and a supply of chemicals, some of them unusual, which in view of the immediately following post-war scarcity reminds one of Joseph's store of corn laid up against the Egyptian famine. Loyalty to his friends and associates marked Professor Gooch's years of university activity, as all who have worked with him will testify.

Conservative by nature, he keeps fully informed of the progress of chemical science, but does not without careful consideration turn to newly propounded theories. He has always insisted upon the importance of comprehensive study of chemical phenomena along the lines of descriptive chemistry. His retiring disposition has kept him from gatherings of chemists where his presence would have been much appreciated.

His loyalty to local journals has resulted in giving his published work and possibly that of his students less publicity than might have resulted had these papers appeared in the more widely circulated chemical journals. He finds great pleasure and relaxation in the reading of good fiction and in genealogical research. A recent statement in a prominent New York newspaper to the effect that chemists are as a class fond of cats may be disputed, but certainly the feline race has no better friend than Dr. Gooch, nor one more convinced of its intelligence.

His former pupils always love to call on him when in New Haven and talk over their laboratory days and discuss their current problems. His fund of reminiscence is rich, as is also his collection of good stories, and we all enjoy them both, for together with his keen analytical mind he has a rare sense of humor.

Philip E. Browning

NOTES AND CORRESPONDENCE

Shortening—Its Definition and Measurement

Editor of Industrial and Engineering Chemistry:

The writer has made shortening measurements with the shortometer [This Journal, **3**, 79 (1921)] for the last six years and has only recently checked up these measurements, and in no case can he substantiate the conclusions made in the article by Platt and Fleming [This Journal, **15**, 390 (1923)], entitled "The Action of Shortening in the Light of the Newer Theories of Surface Phenomena."

The following series of all shortening measurements is a fair evaluation of the various fats and oils:

> Lard, which has the greatest shortening power, naturally comes first. Compounds rank next, and they have about the same shortening power if they are made by adding oil to animal stearin or to vegetable stearin—namely, hydrogenated vegetable oil. Butter fat follows next in order. The oils cottonseed, peanut, olive, rapeseed, soy bean, and corn, all have approximately the same shortening value, which is about three-fourths of the value of ordinary lard.
>
> Coconut oil is somewhat lower than the previous group of oils and has about two-thirds of the value of lard. Coconut oil if broken up into olein and stearin fractions shows a value higher than whole coconut oil for stearin, and lower for olein.
>
> The iodine number of the whole oil is about 9, that of the stearin about 4 or 5, and that of the olein about 16 or 18. It is evident in this case that the fat with the higher iodine number has the least shortening value.
>
> A liquid paraffin oil with an iodine number of 0.4 has a shortening value very close to that of coconut oil. A sample of white vaseline had a shortening value fully as good as the ordinary oils, or 75 per cent of that of lard.

A little difficulty is experienced in using liquid paraffin oil in baking because the high temperature of baking causes the oil to smoke appreciably and loss is thereby experienced.

The writer has very definitely shown in his original article that hydrogenation of an oil increases its shortening value. The iodine number is very materially decreased; yet the shortening value has increased, which is also at variance with their theory.

All the figures available on the shortening value of oils and fats show no definite relationship between shortening value and iodine number.

Clarke E. Davis

National Biscuit Company
New York, N. Y.
June 22, 1923

……

Editor of Industrial and Engineering Chemistry:

This criticism seems to be based upon a misunderstanding of the article by Platt and Fleming. For example, Davis says:

> All the figures available on the shortening value of oils and fats show no definite relationship between shortening value and iodine number.

In this statement we can entirely agree with him, for our article states:

> The iodine number as such cannot be taken as an indication of the shortening power from this point of view, since glycerides of linoleic acid containing two double bonds (Iodine No. 173) do not cover any greater surface than glycerides of oleic acid containing but one double bond per molecule (Iodine No. 86). For this reason, other factors being equal, shortenings should be arranged in the order of their percentage of unsaturated glycerides.

Once it is clearly understood that it is the percentage of unsaturated glycerides and not the iodine number that must be considered, it is seen that Davis' shortening values fit in well with the theory which we have advanced.

Considering first oils only, we find that cottonseed, peanut, olive, rape seed, soy bean, and corn oils, all consist principally of unsaturated glycerides with a small percentage of saturated glycerides which varies with different samples of the same oil. We are not surprised, therefore, at Davis' statement that they "all have approximately the same shortening value." Coconut oil, which has a noticeably smaller proportion of unsaturated glycerides, has noticeably less shortening power, while liquid paraffin, with the smallest proportion of unsaturated compounds, is properly at the bottom of the list of oils in shortening power.

We would invite attention also to specific statements in our paper to the effect that many factors influence shortening power. We state:

> Many factors are involved in the action of shortening.* * * It is evident that no one property can possibly explain the whole action of shortenings.* * * Viscosity evidently plays a part.* * * The melting point is also a factor.* * * A somewhat related quality is plasticity.* * * A fat that will remain plastic throughout the mixing has much greater shortening power than one that is either solid or liquid.

It would seem to be self-evident that these factors would have to be considered in arriving at the shortening power of fats not liquid. It is strictly in line with our theory, however, that lard, etc., containing a considerable percentage of unsaturated compounds, should have greater shortening power than vaseline containing practically none.

On the basis of the statements in our paper it is manifestly impossible to expect the relative shortening power of the "olein" and "stearin" fraction of a shortening to be given simply by their proportion of unsaturated glycerides, as differences in melting point, plasticity, etc., introduce other variables in such a case. The same may be said in comparing the shortening power of a fat before and after hydrogenation.

Davis' findings regarding shortening power are, therefore, not incompatible with our conclusions.

Washington Platt

Merrell Soule Company
Syracuse, N. Y.
September 14, 1923

Calendar of Meetings

Technical Association of Pulp and Paper Industry—Appleton, Wis., October 25 to 27, 1923.

Association of Official Agricultural Chemists—39th Annual Convention, Washington, D. C., November 19 to 21, 1923.

American Institute of Chemical Engineers—Winter Meeting, Washington, D. C., December 5 to 8, 1923.

WASHINGTON NOTES

Nitrite of Soda Hearing

The Tariff Commission held a hearing on the costs of sodium nitrite in Washington on September 10. Only one witness, C. F. Graff, president and general manager of the American Nitrogen Products Co., Seattle, Washington, appeared before the commission. He argued for a 50 per cent increase in the 3 per cent duty on this product, or an increase from 3 cents to $4^{1}/_{2}$ cents per pound. His application was opposed by counsel for the Norwegian Nitrogen Products Co., New York, N. Y., the American sales agents for the Norwegian product. Mr. Graff stated that his company produced about one-half of the domestic output of sodium nitrite, and that the capacity of all the plants of the United States was sufficient to fully meet the domestic requirements. The Norwegian company presented no cost figures. The hearing was continued until September 26 at which time final arguments will be heard. Meantime, it is believed that ample time will be available for the filing of the necessary briefs.

Since the hearing of September 10 the commission has issued a summary of information in the matter of sodium nitrite. This summary consists of information obtained from the public hearing, from publications, correspondence on file in the Tariff Commission, questionnaires sent to manufacturers, and inspection of books and factories of manufacturers by representatives of the commission, and interviews with persons having personal knowledge of this industry. All information in regard to manufacturing costs of individual firms and other information in the nature of trade secrets of processes has been eliminated from this summary, as required by Section 708 of the Revenue Act of 1916.

Improved Cassina Beverage

George F. Mitchell, supervising tea examiner of the Bureau of Chemistry, has developed a new process for making the beverage cassina which eliminates the former "herbish" taste, to which there was some objection. Mr. Mitchell has recently returned from South Carolina where he has been operating the experimental cassina factory which began work last spring. Those who have sampled a hot or an iced drink made from the new processed leaves are enthusiastic over its qualities as a palatable and refreshing beverage. It has a flavor and a stimulating effect that are believed to be distinct commerical assets.

A flavoring extract has also been prepared from the new processed leaves. This extract has been used by the Department of Agriculture to flavor ice cream and the finished product is said to have met with favor. So concentrated is the extract that one tablespoonful will flavor a gallon of ice cream and only 2 cc. are necessary to flavor a carbonated drink.

One decided advantage of the cassina plant is that all the leaves may be used, since they all contain caffein. Tannin, however, is present in a less degree in cassina than in similar beverages.

Sodatol for Distribution

Eighteen million pounds of sodatol, a surplus war explosive, are to be distributed by the Bureau of Public Roads, United States Department of Agriculture, for road-building and land-clearing purposes. The new supply of explosive is very similar to dynamite and picric acid, 12,000,000 pounds of the latter having already been distributed to road-builders and farmers.

Better Lime

Experiments conducted at the Bureau of Standards have shown a way to improve the manufacture of hydrated lime so that the grade known as "finishing" hydrate is regularly produced instead of the grade known as "masons" hydrate, which because of its lesser plasticity commands a lower price. These tests have shown that plasticity depends not alone upon the colloidal content of the hydrate, but upon the effect on this colloid of the manufacturing process.

It has been found that the drying out can be prevented by letting the freshly made hydrate cool in an atmosphere of steam, while flocculation can be prevented by adding small amounts of a readily soluble calcium salt. A hydrator designed to apply these principles has just been completed for further experiment.

September 18, 1923

Personals

Benjamin Alderson, formerly chemist for the American Bottle Co., Streator, Ill., and since February general factory foreman of the company's Newark, Ohio, plant, has been transferred to the Streator factory and promoted to assistant plant manager.

C. Scott Althouse, president of the Althouse Chemical Co., Reading, Pa., is spending about two months traveling through the industrial districts of England, Scotland, France, and Germany.

S. Henry Ayers, formerly bacteriologist of the dairy division of the Bureau of Animal Industry, Washington, D. C., has been appointed director of research of the Glass Container Association.

L. H. Baekeland, honorary professor of chemical engineering in Columbia University, has been made an officer of the Legion of Honor (French) and of the Order of the Crown of Belgium.

J. P. Bonardi, formerly manager of the Assay and Chemical Department of the Mine & Smelter Supply Co., Denver, Colo., has been promoted to sales manager of the New York office, with headquarters at 42 Broadway.

Walter D. Bouner, who has been absent from the University of Utah during the past year on sabbatical leave, has returned and will resume his duties as professor of chemistry at that university.

S. Caplan, formerly research chemist for the Nucoa Butter Co., Bayonne, N. J., has joined the research staff of the Combustion Utilities Corp., Long Island City, N. Y.

John P. Crabb, a recent graduate of the Massachusetts Institute of Technology, is at present employed in the Gas Division of the U. G. I. Contracting Company of Philadelphia, studying the design of the standard water-gas apparatus of this company.

Ellery K. Files, chemical engineer, who has been connected with the Duratex Corporation for over three years, has been given entire charge of manufacture in the plant in Newark, N. J.

The University of Strasbourg has conferred the title of doctor (honoris causa) on **Simon Flexner** and **Jacques Loeb,** of the Rockefeller Institute of Medical Research, and on **William H. Welch,** of the Johns Hopkins University.

Herbert L. J. Haller, associate chemist, who has been on the staff of the Bureau of Chemistry since 1919 and assigned to the Color Laboratory, has resigned to accept a position with the Rockefeller Institute.

M. E. Holmes has resigned as chemical director of the National Lime Association, and accepted the position of development engineer in charge of research for the U. S. Gypsum Co., 205 W. Monroe St., Chicago, Ill.

Ivar N. Hultman has been appointed chemist in charge of operations at the Kingsport plant of the Tennessee-Eastman Corporation.

M. L. Jackson has accepted a position as research chemist for the Piron Coal Distillation Systems, Inc., Detroit, Mich.

The deaths are announced of **F. Krafft,** professor of chemistry at Heidelberg, aged seventy-one, and **Josef Nevinny,** professor of pharmacology at the University of Innsbruck, aged seventy years.

H. A. Kuhn, who has been chief of the department of toxicology of the Chemical Warfare Service for the past four years, has been detailed to the University of Wisconsin for a year for a special course in toxicology under A. S. Loevenhart.

Rex McDill, who has been spending some time in Cuba in research work on the dehydration of fruits, has returned to Riverview, Fla., to continue his researches.

(*Continued on next page*)

PARIS LETTER

By CHARLES LORMAND, 4 Avenue de l'Observatoire, Paris, France

SALE OF REPARATIONS DYES

In the first month of 1923 the French government seized in the Ruhr, by right of the reparations, an important stock of dyestuffs from Badische, Meister Lucius, and Chemische Fabrik. This stock contained about 7000 tons, and the French government, in agreement with the Belgian government, has just decided to put the stock on sale. It is composed chiefly of indigo and alizarin. Since all these products are already being manufactured in France, the sale for exportation will only be permitted if it does not interfere with French and Belgian producers. The dyestuffs not manufactured in France or Belgium, and existing in the lot seized, will be distributed according to priority among the producers in these countries. This sale will certainly have an effect on the dyestuffs market and may bring about a temporary disturbance.

NEW METHOD OF VOLUMETRIC ANALYSIS

MM. Hackspill and Heeckeren have just perfected an original method of elementary volumetric analysis. The substance is roasted *in vacuo*, at a temperature of 800° to 900° C., in the presence of copper oxide. The nitrogen and carbonic acid are collected with a mercury pump and their volume is measured. The carbonic acid is separated by potash. The water produced in the combustion is first separated from the gaseous mixture by condensation at −80° C., and is then directed, in the vapor state, onto the calcium hydroxide. The hydrogen liberated is recovered and measured. Thus, by a single combustion, are obtained, on substances weighing from 2 to 5 cg., three determinations of nitrogen, carbon, and hydrogen.

FUELS

French chemists seem to be directing their attention just now to the study of fuels. M. Piettre has studied the transformation of the coal in humus. The product of oxidation was reduced by a reaction similar to that which permits the transformation of benzine, first into a nitro compound, and then amine (aniline). The product finally obtained was similar to the humus.

M. Paul Lebeau has undertaken the study of the gas formed by the carbonization of solid fuels. Previously, Picter, of Geneva, examined the liquid products obtained by the distillation of combustible liquids in a vacuum. M. Lebeau's method permits the determination, for temperatures from 100° to 1200° C., increasing by fractions of 100 degrees, of the composition of the gas obtained in heating *in vacuo* anthracite, wood, peat, and lignite. Each of these types of fuels gives, by its increasing decomposition, the gaseous volumes which seem sensibly constant for each of the kinds of fuels studied. The total volume of gas formed is estimated at between 150 and 170 cubic meters per ton for the wood, 266 cubic meters for the peat, 228 to 240 cubic meters for the lignite, and 257 to 309 cubic meters for the anthracite.

The analysis of the gas liberated furnishes very interesting results, since the largest part is composed of hydrogen. A ton of English anthracite, for example, gives, at 1200° C., 318 cubic meters of gas composed of 291 cubic meters of hydrogen, or 91.4 per cent. There is no connection between the volume of gas liberated and the content of volatile matter in the fuel considered. Certain anthracites give volumes of gas just as great as the fatty oils, which contain larger quantities of volatile matter than the anthracites. The other constituents of the gas are carbon dioxide and carbon monoxide, with small quantities of metal. One might consider that the carbonization of the anthracite would constitute a source of hydrogen capable of being used in the manufacture of synthetic ammonia.

M. Maihle, continuing work on the production of petroleum by decomposition of vegetable oils, has shown that it is possible to use chloride of zinc as a catalyst in the hydrogenation. On heating different vegetable oils (peanuts, castor) or animal oils (requin, whale) with fused zinc chloride, the liberation of acrolein was accomplished and products boiling between 110° and 310° C., composed of a mixture of methane and ethylene hydrocarbons analogous to petroleum, were formed. Chloride of magnesium gives similar results.

ESTIMATE OF THE VALUE OF FERTILIZER

I suggested in a previous letter that it would be interesting to estimate the increase of efficiency of plants under the action of various fertilizers, and I mentioned that the determination of sugars or of other principal constituents would give the most precise results.

M. Blaringhem, professor at the Conservatory of Arts and Measures, proposes using a method which is purely biologic and founded on genetic experiments. He took crops of barley, linen, and poppies. He subjected them to the action of various fertilizers: potash, nitrogen, phosphoric acid, limestone; then he weighed the test plants and the treated plants—for the barley, the proportion between the length of the third mark under the head and that of each corresponding—for the linen, he measured the thickness of the foliage, that is, the distance between each leaf on the same part of the stalk. He found, for example, that in the last case the foliage density, which was 11 to 12 for the test plants, equaled 16 for the linen subjected to potash fertilizer, and 24 for the linen subjected to nitrogen fertilizer.

. . . .

The Third Congress of the Society of Chemical Industry will meet in Paris, from the 20th to 25th of October. It will be particularly devoted to the agricultural applications of chemistry.

August 30, 1923

Personals (*Concluded*)

F. A. McMillin has resigned his position on the staff of the chemistry department of the University of Washington to take charge of the department of chemistry at the Idaho Technical Institute, Pocatello, Idaho.

A. A. Orlinger has resigned his position as chemical engineer and assistant chief chemist of the Henry Souther Engineering Co., Hartford, Conn., to become chemical engineer and chemist for the Warren Manufacturing Co., with headquarters at Milford, N. J.

V. F. Parry, formerly of the Pittsburgh station of the Bureau of Mines, is now a research chemist for the Combustion Utilities Corp., Long Island City, N. Y.

Arthur E. Rice, president of the Pennsylvania Salt Manufacturing Co., Philadelphia, Pa., died suddenly August 26 at the Canyon Hotel, Yellowstone Park, where he was spending a vacation. He was fifty-two years of age.

Elliott S. Robinson has been appointed assistant director of the Division of Biologic Laboratories of the Massachusetts State Department of Public Health.

E. S. Stateler has recently resigned his position as an Industrial Fellow at Mellon Institute to do research and developmental work for Hershey Brothers, manufacturers of chocolate, in Pittsburgh, Pa.

V. H. Wallingford, who recently returned from a year's study and travel as a fellow of the Commission for Relief in Belgium Educational Foundation, has accepted a position as research chemist with the Mallinckrodt Chemical Works, St. Louis, Mo.

W. C. Weltman, formerly chemist for the State of Illinois, is now first assistant chemist for the St. Louis, San Francisco Railroad Co., Springfield, Mo.

George Wilson, formerly instructor of chemistry at Purdue University, Lafayette, Ind., is now employed in the Research Bureau of the Aluminum Company of America.

N. E. Woldman has resigned his position as instructor of electrochemistry at the University of Maine, to accept an assistantship in the department of chemistry of the University of Illinois, where he will continue his studies for his doctor's degree. Mr. Woldman was formerly secretary-treasurer of the Maine Section of the American Chemical Society.

GERMAN LETTER

By Herr Hobein, Ebenhausen bei Munchen, Bayern, Germany

Extended Patent Rights

A German law of 1920 specifies that rights of patents and copyrights which could not be worked during the war can be extended beyond their legal duration. Accordingly, the interval from August 1, 1914, to July 31, 1919, is not reckoned in the legal duration of a patent. At the same time the law grants to anyone who between the expiration and extension of a patent right has made use of the recently freed invention, the continued use without a license.

As to whether an unlicensed continuance should be allowed to one who had already worked the invention before the expiration of the patent right under infringement of the same and had continued in it afterward, there were different opinions. Through a decision of March 17, 1923, the court has now decided in favor of the inventor, in that it denies to the patent infringer the right of unlicensed continuance.

Hans Goldschmidt

Prof. Hans Goldschmidt, well known in scientific and technical circles, leader and promote of the Chemischen Fabrik Th. Goldschmidt A.-C. in Essen, died on May 31, at the age of sixty-two years. His most important accomplishment was the perfection of the Thermit process, which has found its greatest use in the welding of rails and tubes, and the mending of broken parts of machinery. It is based on the great heat of reaction which aluminium develops in burning to aluminium oxide, whereby the heavy metal oxides such as iron oxide lose oxygen, and are reduced to a molten metal. Through the aluminium-thermo process it was first possible to prepare chromium, manganese, molybdenum, and their compounds such as ferrochrome, ferrovanadium, etc., pure and free from carbon. The Franklin Institute has honored Dr Goldschmidt with the Elliot-Cresson Medal.

New Developments in the Lead Chamber Process

In spite of the introduction of the contact process for the production of sulfuric acid, the lead chamber process continues to hold its place. The repeated successful attempts to make it more profitable are directed toward limiting the large requirement of lead which the construction of the chambers requires and the large amount of necessary space, at the same time procuring conservation or increase of efficiency.

An excellent solution of the problem for the past fifteen years has been the approved Opl-tower system. It uses, instead of lead chambers, trickling towers, and in place of nitrous gases the quickly reacting liquid nitrous acid. The latter has been used also for several years in connection with the centrifugal-drum process of Schmiedel-Klencke. It is a characteristic of this process that the nitrous acid is brought by means of plunging, rapidly rotating drums into very intimate contact with the sulfur dioxide gases. In this way a very complete and quick absorption is accomplished. The process is especially valuable for the preparation of roasting gases with low and varying content of sulfur dioxide.

In a recent article in *Chemiker Zeitung*, Herr Opl, the inventor of the first-mentioned tower process, recommends taking a further step and constructing trickling towers of single iron tanks. This metal is not attacked by 50 to 60-degree acids. In six vessels of about 4 cubic meters volume, connected one behind the other, the formation of sulfuric acid is said to be effected in such a manner that the roasting gases under certain conditions may be converted into nitric acid. With such a system of six iron vessels Herr Opl obtains the same efficiency as with a normal-sized tower system taking ten times the amount of space.

Research on Chlorination Processes

Chlorine roasting consists, as is well known, in heating copper ores with the addition of alkali or alkali-earth chlorides in the presence of air, by which the copper is changed into a water and acid-soluble form consisting of a mixture of chloride, sulfate, and oxide. This process is especially adapted for manufacture from very poor ores or copper waste. Professor Tafel, in Breslau, has recently completed systematic research on this process and gave a report of it at the convention of German smelters and miners. His work is at present limited to the behavior of copper sulfide, the most important constituent of copper-containing iron pyrites waste, for whose preparation in Germany the chlorine roasting is used.

The results are important for the theory and practice of the process. It has been shown that it is not usually necessary to attain the previously prescribed temperature of 500° to 600° C. Moreover, one of 350° to 375° C. is considerably more favorable. The theoretically required quantity of chlorinating material is given in the proportion of 1 part copper, 1 part chlorine—for example, $Cu_2S : 2NaCl$. Potassium and calcium chlorides work more energetically than sodium chloride. In order that the addition of acid may not be needed air is admitted in small quantity. Steam is not necessary for bringing about the reaction, neither is the presence of iron.

Hints as to the Durability of Lead Containers

It often happens in chemical industries that lead containers are attacked by acids, while the same lead material will resist the same acids at equivalent temperatures in the laboratory. Herr Salvisberg points out in *Chemiker Zeitung* that galvanic currents may be the cause of this corrosion. The possibility of their origin through the contact of the two metals is suggested, as this is the case with lead-covered iron containers. In order to remedy this difficulty the apparatus should either be completely insulated so that no contact with the earth can take place, or, if this is not possible, the current strength and potential drop through the conductor should be determined by instruments, and an equal opposite current sent through the apparatus. The result is said to be surprising.

New Method of Titrating Silver and Halogen Ions

Concerning this subject Professor Fajans, of München, has written considerable, and recently has delivered a lecture before the convention of the German Bunsen Association for Practical Physical Chemistry. He has found that if to a very thin, green fluorescent solution of sodium fluorescein and alkali chloride, bromide, or iodide, is added gradually silver nitrate, in exceeding the equivalence point a sudden change to a red color occurs. On back-titrating with a very small excess of halogen ions the original color is recovered. Similarly, the halogen substitution products of the fluorescein can be used as indicators. The phenomenon is based on the fact that the colloidal silver halide portions adsorb the excess silver halide ions, To the silver ions of the silver halides and especially to the adsorbed excess silver ions can be added the dyestuff anions, and the red colors peculiar to the undissociated salts of these dyestuffs result. By adding excess halogen ions the dyestuff anions at the surface can be precipitated.

News of the Dye Industry

Professor Kalb, of München, announces that the shade of a dye, with other properties, can be frequently changed with profit. For example, from the usual reddish blue indigo is obtained pure blue and greenish blue chlorine and bromine derivatives. It is now possible, through high "iodination," to change the color of indigo still more, so that a pure green is obtained. The product obtained by the halogenation of indigo to green is of particular interest because only a very few green vat dyes are generally known. A simple process could be worked out for the production of high-iodinated indigoes.

New Processes of Microsublimation

A very simple device is described by Professor Kempf, of Berlin, in the *Zeitschrift für analytische Chemie*. The substance to be sublimed is heated in a very thin layer on an electric hot plate, the temperature of which is accurately regulated and can be kept constant within one degree. The sublimate is collected directly on the slides, which are placed immediately on the sublimation material. The apparatus can also be used in a vacuum and permits the microphotographical rendering of the sublimate.

August 6, 1923

BOOK REVIEWS

Atomic Structure and Spectral Lines. By ARNOLD SOMMERFELD. Translated from the third German edition by HENRY L. BROSE. xiii + 626 pages. E. P. Dutton & Co., New York, 1923. Price, $12.00.

The first German edition of this book was published in 1919, and contained 550 pages. The fact that this work has passed through two editions in a relatively short time is sufficient evidence of its popularity even in the original German form. The need of translating this monumental work into English has been felt for some time, and undoubtedly the present translation will be welcomed by a very large number of scientific men in England and America. The translator is to be complimented upon his work. Only on rare occasions does he slip into German idiom, but, on the whole, he has succeeded in producing an extremely readable work.

Nothing can indicate better the rapidity of progress in the particular realm of science which is the subject of the present work than the fact that almost three-quarters of it are devoted to a discussion of developments during the past decade. Bohr published his first paper in 1913, and in the same year Laue carried out his epoch-making investigation on the nature of X-rays. The various physical phenomena and theoretical speculations discussed by Sommerfeld may be regarded as originating largely in the discoveries of these two investigators.

The first two chapters are devoted to an excellent and yet concise discussion of such topics as the nature of cathode rays, canal rays, alpha and beta rays, the theory of X-rays based on classical electrodynamics, radioactive phenomena, nuclear charge, the periodic law, and theory of isotopes. The photo-electric effect is described and the author is thus able to introduce the experimental evidence obtained by Millikan and his collaborators for the validity of Einstein's law ($V\epsilon = h\nu$) and the existence of the quantum constant h. (This method of introducing the beginner to the quantum theory has always appealed to the reviewer as much simpler than the classical method which involves an abstract discussion of Planck's radiation laws.) Sommerfeld also points out that Bohr's fundamental equation $h\nu = W_e - W_a$ is the counterpart of Einstein's law.

The third chapter, X-ray Spectra, contains a discussion of the methods of measuring wave lengths and characteristic lines. In the fourth chapter the author shows that the quantum hypothesis may be expressed in the form of the postulate that the phase integral must be a whole multiple of the quantum of action h. Bohr's theory of the spectrum of hydrogen and ionized helium and the extension of this theory to include elliptic orbits are discussed very fully.

The fifth chapter contains a discussion of the most recent development in the quantum theory of spectral series, such as the principles of selection and correspondence, the application to Stark and Zeeman effect and the adiabatic hypothesis.

The quantum theory of series spectra in general is taken up very fully in Chapter VI, and shows how Bohr's theory has given us an interpretation of a vast amount of data so carefully compiled by spectroscopists and, by means of the relation of these to ionization and resonance potentials, has led to a deeper understanding of atomic structure. This marvelous success of a bold speculation will rank as one of the most epoch-making achievements in the history of science.

Chapter VII is devoted to the quantum theory of band spectra, and in Chapter VIII the author discusses his theory of the fine structure of spectral lines. The greatest interest attached to this theory is the fact that it furnishes experimental evidence for the Einstein theory of relativity.

While the author has not hesitated at the use of mathematical derivations in connection with the different topics, he has wisely kept out the more difficult mathematical treatment in each case and added this in the form of copious notes at the end of the volume.

While this work covers, to a certain extent, the same ground as that already covered so well by Foote and Mohler in their volume on "The Quantum Theory of Spectral Series," the reader will find in it an extremely valuable supplement to the latter.

SAUL DUSHMAN

The Manufacture of Acids and Alkalies. By GEORGE LUNGE, Ph.D. Completely revised and rewritten under the editorship of ALEXANDER CHARLES CUMMING, D.Sc.

Vol. I. Raw Materials for the Manufacture of Sulphuric Acid and Sulphur Dioxide. By WILFRID WYLD. xvi + 542 pages. Illustrated. D. Van Nostrand Co., New York, 1923. Price, $10.00.

Vol. V. The Manufacture of Hydrochloric Acid and Salt-Cake. By A. C. CUMMING. xvi + 424 pages. Illustrated. D. Van Nostrand Co., New York, 1923. Price, $8.50.

"Sulphuric Acid and Alkali," by George Lunge, has frequently been referred to as the "Bible of the heavy chemical industry." Originally published in 1879, it has from time to time been revised, extended, and brought into line with new developments in the manufacturing art.

The position of Dr. Lunge as a compiler of books on heavy chemical manufacture was somewhat different from other authors of similar works. Dr. Lunge had been a chemical manufacturer, and later professor and professor emeritus in the Federal Technical University, Zurich. He was an indefatigable reader and collector of data, and carried on an extensive correspondence with prominent men in the industry.

The place of "Lunge" in heavy chemical literature was therefore unique, and each new edition was a matter of considerable interest to chemical technologists because of the certain appearance of descriptions of new plants and processes.

After Dr. Lunge's death the question of his successor became a matter of great interest to the industry, and the appearance of the first volumes has therefore been awaited with some eagerness and curiosity.

The new editor, A. C. Cumming, has a difficult problem, and his method of attack is best illustrated by the following paragraphs from the Editor's Preface:

> It is doubtful if any one man could take up Dr. Lunge's task of describing adequately all the industries now dealt with in these volumes and it is certain that few would care to attempt it. Each volume will therefore be on a special subject and dealt with by a separate author who is responsible for that volume and is given a wide discretion in his treatment of the subject.
>
> The editor trusts that these united efforts will produce a new edition worthy of the great tradition which Dr. Lunge has established.

In effect, this apparently means the passing of "Lunge," as it has been known, and the appearance of a complete new work related only by title to the original.

Whether this new "Lunge" will some day occupy the position of Dr. Lunge's own work, cannot be decided on the first two volumes alone. The advertising pages at the end indicate that seven volumes are in preparation, with others to follow, so final judgment of the effort must await its completion.

Mr. Wyld's contribution to the series, "Raw Materials for the Manufacture of Sulphuric Acid and Sulphur Dioxide," follows the outline of Vol. I, Part 1, of the fourth (1913) edition of "Lunge." The historical preface and the properties of the raw materials are not greatly changed, but the rest of the matter has been brought up to date. Statistics were evidently compiled, as far as available, up to 1922, so they give a picture of the status and use of the raw materials of the sulfuric acid industry before, during, and after the World War.

There are some evidences of incomplete revision in the form of conflicting statements, as, for instance, on page 162: "Many years ago several works ran their nitre as a solution in water into the chambers. This has long since been discontinued* * * no independent favorable testimony has been published* * *," and on page 164, "According to the 50th Report of the Alkali Inspector, the application of a solution of nitrate of soda* * * to the first chamber has answered very well."

Interesting details of the supply of nitrogen oxides to chamber plants through oxidation of ammonia are given on pages 166 to 175. The statement on page 174 that this process had replaced "plotting" at all the works of the United Alkali Company (in England) should encourage trial installations on chamber plants in this country.

The chapter on pyrites burners is much more complete than the similar chapters in earlier "Lunges," doubtless because of Mr. Wyld's familiarity with mechanical furnaces.

Taken altogether, the new volume is a creditable piece of work, which displays throughout its 542 pages a painstaking effort to follow Dr. Lunge's practice and incorporate everything worth while.

Vol. V, "The Manufacture of Hydrochloric Acid and Saltcake," has been produced by the general editor, A. C. Cumming. It replaces Vol. II, Part 1, of "Lunge," but does not follow the same order of treatment of the subject. The last edition of Lunge, Vol. II, Part 1, was published in 1909, so there was a definite need for a revised edition incorporating the developments of the last fifteen years.

The first few pages of Dr. Cumming's volume bear evidence of a set task to be fulfilled as soon as possible. No other explanation would fit the inclusion of statistics on salt production and consumption exactly as in the 1909 "Lunge." Dr. Lunge gave his figures up to 1907. Dr. Cumming does not add any figures beyond 1907, and as the same wording appears, there is no suggestion of a desire to present current material, but rather the easy use of paste and shears.

In glancing through parallel pages of "Lunge" and Dr. Cumming's, the paste and shears become more evident. New material is so conspicuously absent that on arriving at page 188 a feeling of relief results from the sight of a drawing and descriptive matter of Six and Guttmann's mechanical saltcake furnace, not included in "Lunge."

The author had a chance to present new material on condensation equipment, direct manufacture from chlorine and hydrogen, and to give details on bulk movement of the acid in wood and rubber-lined metal, tank cars, but all these opportunities were passed over.

The theory of cooling and absorbing hydrochloric acid has received more attention in Dr. Cumming's volume, but even this phase has not been brought entirely up to date.

Mr. Wyld's volume is a contribution to the literature of the heavy chemical industry, but Dr. Cumming's "Hydrochloric Acid and Saltcake," in the reviewer's opinion, is not a worthy successor to Vol. II, Part 1, of "Lunge"—in fact, there does not appear to be much justification for its publication. It would seem to have been a more desirable policy to postpone the preparation of this particular volume until an author was found familiar with the subject and willing to take pains in collecting and presenting information.

A. E. Marshall

Forest Resources of the World. Vols. I and II. By Raphael Zon and W. N. Sparhawk. xiv + 997 pages. McGraw-Hill Book Co., Inc., New York, 1923. Price, $12.00.

We frequently see estimates of the amount of standing timber left in this country, the rate at which it is being cut and the rate at which new timber is growing. This publication is, however, the first in which complete information of this sort has been gathered together to cover the forest resources of all countries. The information given is not entirely statistical, but the character of the forests, the uses of the wood, and the general status of public and private forestry are discussed for each country. Typical headings for the arrangement of the information on the forests of each country are as follows: Forest Area, Character of Forest, Character of Ownership, Annual Cut, Annual Growth, Domestic Consumption, Exports and Imports, Wood-Using Industries, Forestry Education, Forest Laws, and Probable Future. In many cases the figures given are only estimates, but the amount of detailed information which has been gathered in regard to the forests of the world is surprisingly large.

The book is easy to read and the style is sufficiently varied to prevent it from becoming a monotonous repetition of statistical information. A series of new colored maps are provided, by which the character and location of the forests of different sections can be rapidly determined. These maps alone give more information on the general subject than has been gathered together into one previous publication.

The main part of the work of direct interest to chemists is the ninth chapter, Forest Resources Other than Timber. In this chapter the subjects of pulp and paper, resins, naval stores, rubber, tanning materials, dyewoods, cork, wood distillation, edible products, and vegetable oils are briefly discussed from the standpoint of statistics and supplies of raw material. This is not, however, the only place where these subjects are mentioned, since in every case where a country is important as a producer of chemical raw materials from the forests these materials are discussed under the heading of the wood-using industries of that country. To the chemist, therefore, the book will be of chief interest in giving complete and detailed information on the source of the chemical materials which come from the forest.

L. F. Hawley

Heat Transmission through Walls, Concretes, and Plasters. By Ezer Griffiths. 33 pages. H. M. Stationery Office, London, 1923. Price, 1s. 6d., net.

This pamphlet is a publication of the Building Research Board, Department of Scientific and Industrial Research of England, It gives a description of apparatus used and summary of results obtained in experiments conducted by the author to determine the rates of heat transmission through various types of wall construction common in English building practice.

The methods used in investigations are similar to those employed by American investigators. However, the materials reported on are not common to the building construction trade in this country. Therefore, a direct comparison with results obtained by investigators and authorities in this country is of little value.

Appendices are included in the book which describe wall constructions experimented on over an extended period by Norwegian investigators, also a summary of results obtained by a committee appointed by the Academy of Engineering Science, Stockholm, Sweden.

The conclusions laid down as the results of the Norwegian experiments, as well as the principles embodied in a new type of German wall construction briefly described, are interesting and well worth study by those interested in the conservation of heat used for industrial buildings, as well as dwelling houses.

Edgar C. Raek

A Symbol of Safety. By Harry Chase Brearley. xiv + 290 pages. Doubleday Page & Co., New York, 1923. Price, $2.50.

The "Symbol of Safety" is the label of the Underwriters' Laboratories, Inc., and Mr. Brearley's book is a review of the activities and significance of the work of this institution.

In a general way most of us are familiar with some form of equipment carrying the label "Underwriters' Laboratories Inspected," whether it be a fire extinguisher, a valve, a ladder, or even a Christmas tree lighting outfit. We also have a hazy idea (unless our work has brought us into direct contact with the laboratories) that the label means a standard of construction and performance.

The book, while essentially written for the nonscientific reader, gives a clear picture of the development and growth of Underwriters' Laboratories, from a single room and a total force of three in 1893 to a main testing plant occupying 55,000 square feet, two branch laboratories, and employing four hundred and fifty people in 1922.

The story is interesting to the chemist and the engineer, as it shows the gradual appreciation by outside interests of the reliability and value of laboratory testing methods.

The present scope of the testing work of Underwriters' Laboratories will surprise most readers of the book. Certificates of air-worthiness for aeroplanes, rating of automobiles as regards fire hazards, testing of gasoline supply systems, and determination of the ultimate breaking point of building columns under load and conflagration conditions, are some of the unexpected features of the laboratories' operations.

The important position of Underwriters' Laboratories in relation to industry is indicated by the statement that over half a billion labels were issued and applied to inspected equipment in 1922.

The book, despite its nontechnical language, is well and interestingly written. It is free from evident errors and bears internal evidence of careful revision.

The illustrations are remarkably good, and as they occupy 75 pages in comparison to 247 pages of text matter, it would seem that the photographer, following current motion picture practice, should have received title page acknowledgment.

A. E. Marshall

Material Handling Cyclopedia. Edited and compiled by Roy V. Wright, John G. Little, Robert C. Augur, and seven others. 847 pages. Simmons-Boardman Publishing Co., New York, 1921. Price, buckram $6.00; leather, $12.00.

As its name implies, this volume is a complete compendium of information on tools for handling materials. It consists of three distinct sections. The first section is a dictionary of the terms used later, and thus a reasonably complete dictionary of the terms in general use in this kind of work. Probably the most interesting point about this section is that it serves as the general index to the volume. After each definition is noted the page or pages in the later sections on which full discussion of that subject is to be found. This innovation might well be followed by other compilers of such compendia, for certainly it couples the idea directly with its full explanation. However, one unfamiliar with the scheme on which this index is built will search in vain through the book for the customary general index, as the only other one included is a table of contents listing the sections and chapters in the order in which they are treated. The dictionary itself is divided into two parts, one dealing with general terms and the other with electrical terms.

The second section is entirely descriptive of material handling equipment and makes up more than half of the whole book. Here qualified individuals discuss the various phases of the problems met under the following chapter headings: Hoisting Machinery, Package Handling Conveyors and Elevators, Loose Material Conveyors and Elevators, Conveying Machinery Details, Elevators, Trackless Transportation, Industrial Rail Transportation, and Handling Systems.

The third section is devoted to advertising. It is interesting to note the method of handling this material, which, incidentally, is well indexed and cross indexed. The pages are made up in strict conformity with the preceding text section and the only indication of their advertising nature is that the signature of the advertiser appears at the bottom of each page. No typographical displays of any kind are included, and as one glances through the book it is not at all obvious where one section ends and the other begins.

NEW BOOKS

Aluminium Facts and Figures (Vest Pocket Edition). 55 pp. Price, 2s. 6d. The British Aluminium Co., Ltd., London.

Chemical Resistance of Engineering Materials. Marston Lovell Hamlin and Francis Mills Turner, Jr. 264 pp. Price, $5.00. Chemical Catalog Co., Inc., New York.

Chemistry as a Career. A Synopsis of Lectures Given by the Registrar before College Chemical Societies during 1921–1923. Institute of Chemistry of Great Britain and Ireland, London.

Course in General Chemistry, Including an Introduction to Qualitative Analysis. William C. Bray and Wendell M. Latimer. 148 pp. Price, $1.60. The Macmillan Co., New York.

Cultivation of Lac in the Plains of India. Rai Bahadur C. S. Misra. Bulletin No. 142, Agricultural Research Institute, Pusa. 83 pp. Price, Rs. 1 8As. Superintendent of Government Printing, Calcutta.

Dictionnaires Techniques Illustrés en Six Langues. Francais-Allemand-Anglais-Russe-Italien-Espagnol. A. Schlomann. 13 volumes, each devoted to a separate branch of engineering and industry. Dunod, Paris.

Domain of Natural Science. E. W. Hobson. The Gifford Lectures Delivered in the University of Aberdeen in 1921 and 1922. 510 pp. Price, $6.50. The Macmillan Co., New York.

Fundamentals of Organic and Biological Chemistry. Thomas Guthrie Phillips. 260 pp. Price, $2.00. D. Appleton & Co., New York.

Hydraulics for Engineers and Engineering Students. F. C. Lea. 4th edition. 594 pp. Price, $6.00 net. Longmans, Green & Co., New York. A revised and enlarged edition, intended to be of value not only to practicing engineers but to students.

Laboratory Experiments in Chemistry to Accompany Black and Conant's "Practical Chemistry." H. Henry Black. 167 pp. Price, 80 cents. The Macmillan Co., New York.

Materie, Elektrizitat, Energie; Die Entwicklung der Atomistik in den Letzten Zehn Jahren. W. Gerlach. **Vol. VII. Wissenschaftliche Forschungsberichte. Naturwissenschaftliche Reihe,** edited by R. E. Liesegang. 195 pp. Price, 3s. 3d. T. Steinkopff, Dresden and Leipzig.

Mineral Industry of the British Empire and Foreign Countries. Statistics, 1919–21. Tin. Imperial Mineral Resources Bureau. 44 pp. Price, 1s. 6d. H. M. Stationery Office, London.

Neueren Chemotherapeutischen Präparate aus der Chininreihe (Optochin, im Besonderen Eukupin und Vuzin) und aus der Akridinreihe (Trypaflavin, Rivenol). E. Laqueur, assisted by A. Grevenstuk, A. Sluyters, and L. K. Wolff. 90 pp. Price, paper, 3s. Julius Springer, Berlin.

Organic Analysis, Qualitative and Quantitative. E. de Barry Barnett and P. C. L. Thorne. 180 pp. Illustrated. Price, $2.25. D. Van Nostrand Co., New York.

Preliminary Experiments in the Low-Temperature Carbonisation of Coal in Vertical Retorts. Fuel Research Board. *Technical Paper* **7.** Department of Scientific and Industrial Research. 27 pp. Price, 10d. H. M. Stationery Office, London.

Production of Liquid Fuels from Oil Shale and Coal in Australia. R. E. Thwaites. Institute of Science and Industry. *Bulletin* **24.** 62 pp. Government Printer, Melbourne.

Soils, Their Property and Management. T. Lyttleton Lyon, Elmer O. Fippin, and Harry O. Buckman. Rural Textbook Series. 764 pp. Illustrated. Price, $3.25. The Macmillan Co., New York.

Tabelle und Anleitung zur Ermittelung des Fettgehaltes nach Vereinfachtem Verfahren in Narhungsmitteln. Futtermitteln und Gebrauchsgegenstanden. J. Grossfeld. 12 pp. Price, 1s. J. Springer, Berlin.

Text Book of Physics for the Use of Students of Science and Engineering. Parts II and III. Heat and Light. J. Duncan and S. G. Starling. 314 pp. Price, $2.00. The Macmillan Co., New York.

Viscosity of Cellulose. R. D. Report No. 22 (Part III). Price, 1s. 9½d. H. M. Stationery Office, London.

GOVERNMENT PUBLICATIONS

Commerce Reports—August

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

The Hide and Leather Division of the Department of Commerce has received a list of the **tanneries** in the Department of Valle del Causa, Colombia. This list is available to firms registered on the Exporters' Index. (P. 343)

The President of Mexico has signed a decree which exempts from import duties all **petroleum** imported into Mexico for the purpose of refining. This concession is made to assist the Mexican refining industry which has been passing through a severe crisis because of the scarcity of oil coming from the Mexican fields for refining. (P. 351)

The annual consumption of **paraffin wax** in Constantinople is between 1000 and 2000 sacks, of which 75 per cent is supplied by American firms and the remainder by Rumania. The prospects for the future development of the trade in paraffin in Turkey appear to be good. (P. 352)

There is a small but consistent demand for **calcium carbide** in the Colombo consular district, and at present the United States is not on the list of suppliers. (P. 360)

Honduras offers a rapidly expanding market for **paints.** (Pp. 360–1)

The annual report of the Harzgesellschaft shows that in the year 1922, 127 tons of **resin** were extracted. From this amount 88,000 kilos of finished resin and 20,500 kilos of turpentine were obtained. The Deutsche Harzgesellschaft has enlarged its works and has leased new ground and an increased production is anticipated. (P. 361)

The German press is now emphasizing the desirability of concluding an arrangement with Russia to open up the latter's enormous **phosphate** resources and convert the raw material to superphosphate on the ground in chemical plants operated by Germany. (Pp. 361–2)

According to certain German dealers, wages and salaries in Baden have increased to such an extent that certain **chemicals** can be imported at a lower price than it would cost to manufacture them in Germany. Stuttgart dealers claim that prices of chemicals in the occupied areas are approximately 50 per cent lower than in the unoccupied areas. (P. 362)

The use of **calcium carbide** is gradually decreasing in the state of Sao Paulo, Brazil. (P. 362)

Intensified activity on the part of **oil shale mines** owned by the Esthonian government resulted in a considerable increase in the total value of the production in 1922 as compared with previous years. (P. 417)

The exports of **chemicals** and **allied products** from the United States for the first six months of 1923 had an aggregate value of $75,125,022, an increase of 21 per cent over the first six months of 1922 and equivalent to 67 per cent of the total value of $112,836,432 for the entire year 1922, June being the record month. (Pp. 419–22)

An American concern is to build a **kraft pulp mill** in Ontario, Canada, with a minimum daily capacity of 75 tons. The manufacture of kraft paper is a new development in that community and will bring into use a wider variety of woods than has been used. (P. 431)

The importation into Mexico of all **narcotic drugs,** except by the Public Health Department of the government, has been prohibited. (P. 438)

Figures are given showing the new increase in Polish consumption taxes on **mineral oils.** (P. 440)

A new **Swiss carburetor** has been invented with features that permit the use of benzene, gasoline, kerosene, or alcohol, without alteration of the carburetor. (P. 463)

The Japanese **heavy chemicals** and **dyestuffs** market in 1922 is reviewed. It is pointed out that the United States has not held the position which it gained during the war, with the single exception of the trade in sulfate of ammonia. For other heavy chemicals and dyestuffs Japan is now turning to England and Germany, principally because better prices can be had from those countries. (Pp. 465–6)

Statistics are given showing the Canadian production, imports, and exports of **arsenic** in 1921 and 1922. (P. 466)

Interested parties may obtain from the Bureau of Foreign and Domestic Commerce a complete list of the names and addresses of **quinine plantations** in the Netherlands East Indies. (P. 466)

The Chilean Congress is considering the question of having an **international exposition** of products relating to **mining, metallurgy,** and **nitrate** at Santiago in 1924. (Pp. 479–80)

A general feeling of optimism characterizes the **petroleum** situation in Rumania. Production is good and on the whole there is considerable confidence in the situation. (P. 481)

Small quantities of **Cuban motor alcohol** have been imported recently into the Canary Islands for experimental purposes with a view to the introduction of that product there. (P. 483

The construction of the canal through the Coyuca and San Jeronimo lagoons in Mexico is bringing to light an almost inexhaustible supply of **mangrove,** the bark of which is used so extensively in the tanning industry. (P. 487)

It is estimated that the **Swedish wood pulp** production for this year, instead of being normal (approximately 880,000 metric tons), will be about 720,000 metric tons, of which about 535,000 tons will be available for export. Production has been lowered because of labor troubles. (P. 488)

By a recent Mexican decree all products obtained from foreign **petroleum** imported for refining will pay only 15 per cent of the current quotas and will be exempt from the Mexican export duties. (P. 497)

The **Scottish mineral oil industry** has survived the stress of recent years and is now in practically full operation. (P. 537)

Both the import and export trade of the United States in **chemicals and allied products** have been on the upswing during the first six months of 1923. An exact comparison of the import trade with corresponding months of 1922 cannot be made owing to the change in classification necessitated by the alterations in the import schedule. A conservative estimate, however, would place the gain in incoming shipments at over 40 per cent. (Pp. 543–4)

Samples of a **wood fiber,** known in the state of Vera Cruz as "jonote," have been received in the Textile Division of the Bureau of Foreign and Domestic Commerce, and are available for inspection. (P. 551)

In accordance with the Commercial Treaty between Austria and Italy, the latter has agreed to grant **special rates** on the following commodities imported from Austria: articles of copper, nickel, zinc, and their alloys; magnesite bricks; carbonic acid, copper sulfate, ammonium sulfate; varnishes; glue; and pulp for the manufacture of paper. Austria, on the other hand, has agreed to admit the following Italian goods at special rates: olive oil; essential oils, sulfur, boric, tartaric, and citric acids; borax; ammonium sulfate, calcium citrate, copper sulfate; superphosphates; calcium cyanide; and oilseed cakes. (P. 562)

Italy has **modified** her general customs **tariff rates** on the following American products: artificial silk; aluminium and its alloys, essence of turpentine; sodium carbonate; barium chloride; lithopone; chemical fertilizers, including calcium cyanamide and impure nitrate of ammonium; formaldehyde; and organic synthetic colors. (P. 563)

Italy has slightly reduced her customs tariff on American **ferro-alloys.** (P. 564)

Latvia has placed an import duty on **salt.** (P. 564)

All materials and machinery for use in the manufacture of **ether alcohol** within the Republic of Salvador may be imported free of duty. (P. 565)

STATISTICS OF EXPORTS TO THE UNITED STATES

Germany—(P. 466)
  Heavy chemicals
  Dyes and dyestuffs

Canada—(P. 488)
  Wood pulp

Tampico, Mexico—(P. 483)
  Petroleum
  Gasoline

SPECIAL SUPPLEMENTS ISSUED

Algeria
Danzig
Finland
Indo-China
Uruguay
Venezuela

Austrian Trade in Rubber Products. C. H. FOSTER. *Trade Information Bulletin* **131.**

Polish Petroleum Industry in 1922. *Trade Information Bulletin* **135.**

The Brazilian Market for Paper and Paper Products. *Trade Information Bulletin* **127.**

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of the Census

Chemicals and Allied Products. 14th Census of the United States, Manufactures, 1919. Prepared under the supervision of E. F. Hartley. 187 pp. 1923.

Essential Oils. Manufactures, 1921. 8 pp. Paper, 5 cents.

Explosives. Manufactures, 1921. 10 pp. Paper, 5 cents

Pulp-Wood Consumption and Wood-Pulp Production. Compiled in coöperation with the Department of Agriculture, Forest Service. Forest Products, 1921. 13 pp. Paper, 5 cents.

Turpentine and Rosin. Manufactures, 1921. Compiled in coöperation with the Department of Agriculture, Bureau of Chemistry. 10 pp. Paper, 5 cents.

Bureau of Mines

Accidents at Metallurgical Works in the United States during the Calendar Year 1921. W. W. Adams *Technical Paper* **327.** 31 pp. Paper, 5 cents.

Carbon Tetrachloride Extinguisher on Electric Fires. S. H. Katz, E. J. Gleim, and J. J. Bloomfield. *Reports of Investigations* **2499.** 16 pp. Issued July, 1923.

Coal-Mine Fatalities in June, 1923. W. W. Adams. *Reports of Investigations* **2508.** 4 pp Issued July, 1923.

Comparative Tests of By-Product Coke and Other Fuels for House-Heating Boilers. Henry Kreisinger, John Blizard, H. W. Jarrett, and J. J. McKitterick. *Technical Paper* **315.** 21 pp. Paper, 5 cents

Disastrous Inflammation of Coal Dust in Excavating a Mine Dump. C. A. Herbert. *Report of Investigations* **2498.** 2 pp. Issued July, 1923.

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MARKET REPORT—SEPTEMBER, 1923

[Supplied by Drug & Chemical Markets]

Now that the summer is over and the trade looks back on the total volume of business actually consummated, the figures are not nearly as disappointing as the pessimistic reports heard during July and August would have led one to believe. Taken all in all, the volume of business during the summer was not below normal when compared with other years. Of course, in numerous instances prices were too low for a healthy market—that is, where they were below cost of production as a result of seasonal competition. As expected, the middle of September saw some expansion in demands. Buyers, however, do not appear anxious to abandon a policy of caution, with a consequence that the quantity of goods sold on each individual order is usually small, although orders are more frequently repeated.

One of the features of the market late in the month was an announcement of alkali prices for next year by a leading manufacturer. The prices for contracts are the same as those which have been maintained this year and last year. The prices are considered low when the increase in costs of production are taken into account, but the increase in volume of business during the past year to some extent offset the increased costs of production. The steady prices of alkalies have had a stabilizing influence on the chemical market as a whole. Heavy acids have been somewhat routine with the exception of sulfuric acid which has been moving steadily. Lactic acid has been in fair demand. Oxalic acid continues easy owing to lack of demand and competition. All cheap lots of ammonium chloride have been taken up and prices have advanced. Ammonium sulfate has been quiet but demand is expected to open up soon. Export demand for arsenic has kept this item moving better than it otherwise would be, since domestic demand has fallen off after the disappointing season for calcium arsenate this summer. Arsenic has climbed back to 11 cents per pound mainly through the call from European countries. Calcium arsenate is nominal as sellers endeavor to liquidate stocks left over from the past season.

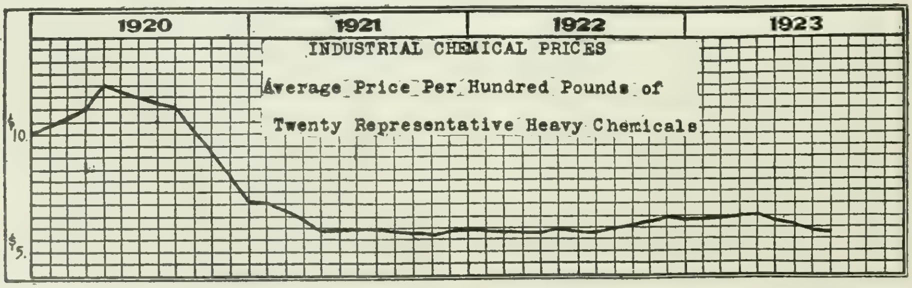
Bleaching powder has become firmer with the approach of cooler weather. Most of the distressed lots have been absorbed and the weakness of the summer months is gradually disappearing. Competition continues keen and prices for the last quarter are still unsettled. Chlorine is settling down to steadier buying as many paper mills resume operations. Demand for barium products has been gaining steadily. The carbonate is sold well ahead and makers' prices have advanced. Imported material is scarce and high owing to the high import duty. Barium chloride demand is improving and some factors are quoting higher prices. Copper sulfate is quiet and prices are inclined to be easy owing to recent declines in metal prices. Potassium chlorate is firm and in good demand. Potassium bicarbonate has made sharp advances because of scarcity abroad. Imported caustic potash is unsettled though no important price changes have occurred. Recent changes in selling for export in Germany have kept the situation unsettled. Potassium prussiates continue quiet and prices are easier. Potassium bichromate has declined owing to slow demand and keen competition. Potassium permanganate is firm with a lone domestic maker competing with imported material.

Sodium compounds have undergone little change in prices or demand. Soda ash and caustic soda are in steady demand. Makers of sodium bichromate are quoting lower prices. Sodium prussiate declined during the month and then recovered again to its former position at 14 cents per pound. Sodium chlorate is firm. Sodium sulfide supplies are plentiful and prices are easy in the face of slow demand. Demand for Glauber's salt has not been active and supplies are not so small as usual for summer months. Tin crystals are higher for September owing to rising metal prices.

Demand for intermediates has begun to show improvement after the quiet period during the summer. Inquiries have become more frequent and orders for small amounts are coming in. Prices have shown little change except in the case of *o*- and *p*-toluidine. Both these products have advanced as demand continued to increase. β-Naphthol has been subject to some competition and sales have been reported below current quotations. Resale lots of intermediates have been few and scattered, and makers have the situation well in hand. Coal-tar crudes have become easier as supplies became more plentiful. Benzene has weakened considerably owing to the recent reductions in gasoline prices. Phenol has declined to a basis of 28 cents per pound at works. Cresylic acid demand has shown an increase and one maker has advanced his prices. Naphthalene continues quiet and prices are soft. Pyridine supplies are difficult to locate and sellers are quoting up to $5.00 per gallon.

Demand for fixed oils, fats, and greases has been showing improvement this month. Animal oils and tallow are higher. Vegetable oils are in better demand and prices are stronger. Fish oils are reported in smaller supply this year and sellers are higher in their views. Turpentine and rosin have been quiet.

Hexamethylene has been reduced by American manufacturers owing to keen competition with the imported material, and now $77^{1}/_{2}$ cents per pound f. o. b. New York is quoted for 100-pound lots and 75 cents per pound for 2000 pounds or over. Holders of imported potassium permanganate have advanced the price to 18 and 19 cents per pound spot in order to feel out the market. Domestic makers are naming $17^{1}/_{2}$ to 18 cents per pound at works. Import cost still remains high and last heard was 16 cents per pound c. i. f. New York. Salicylic acid is quoted at 35 cents a pound spot by makers and resellers are named at 34 cents per pound in limited quantities. The market is reported quiet at the moment. The end of the season has found holders of citric acid well supplied and further reductions in prices are likely.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

INORGANIC CHEMICALS

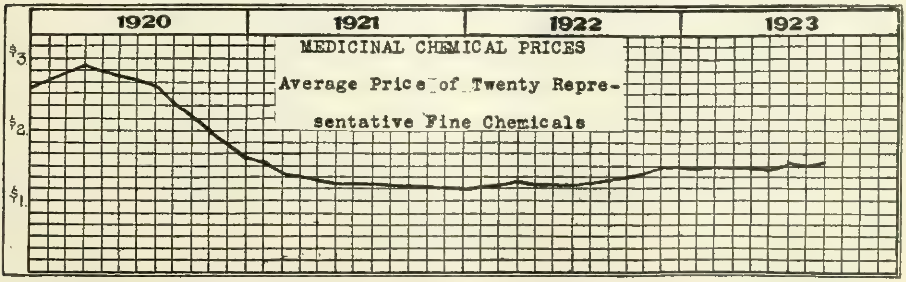
	Sept. 1	Sept. 15	Jan. 1923
Acid, Boric, cryst. bbls.......lb.	.11	.11	.11½
Hydrochloric, comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb.	.65	.65	.65
Nitric, 42°, cbys. c/1 wks.lb.	.05¾	.05¾	.06
Phosphoric, 50% tech....lb.	.08	.08	.08
Sulfuric, C. P...........lb.	.09	.09	.07
66° tks. wks.......ton	15.00	15.00	15.00
Oleum, 20%.......ton	19.00	19.00	18.00
Alum, Ammonia, lump.......lb.	.03½	.03½	.03½
Potash, lump...........lb.	*.03¼	*.03¼	*.03½
Chrome............lb.	.05½	.05½	.05½
Soda, ground...........lb.	.04	.04	.04
Aluminum Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd..lb.	.09	.09	.09½
Chloride, white gran.....lb.	.07½	.07½	.07½
Ammonia, anhydrous........lb.	.30	.30	.30
Ammonia Water, drums, 26°.lb.	.07½	.07½	.07½
Arsenic, white..............lb.	.10½	.11	.15½
Barium Choride............ton	*80.00	*82.50	*92.50
Nitrate................lb.	*.07¾	*.07¾	*.07½
Barytes, white.............ton	33.50	33.50	33.50
Bleaching Powd., 35%, works .... 100 lbs.	1.75	1.75	2.15
Borax, cryst., bbls...........lb.	.05½	.05¼	.05½
Bromine, pure, wks..........lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b. N. Y...................ton	24.50	24.50	24.50
Chlorine, liquid.............lb.	.05	.05	.05¼
Copper Sulfate......... 100 lbs.	5.10	5.10	6.25
Iodine, resublimed...........lb.	4.55	4.55	4.50
Lead Acetate, white crystals..lb.	.14	.14	.13
Nitrate................lb.	.22	.22	.22
Red.............. 100 lbs.	11.40	11.40	10.60
White (Carb.)..........lb.	.09¾	.09¾	.08½
Lime, live and hydrated, bbl..lb.	.01½	.01½	.01½
Oyster shell.............lb.	.03	.03	.03
Lime Acetate.......... 100 lbs.	4.00	4.00	3.50
Magnesium Carbonate, tech..lb.	.08	.08	.08
Magnesite, calcined.........ton	55.00	55.00	55.00
Phosphorus, yellow..........lb.	*.35	*.35	*.28
Red...................lb.	—	—	*.30
Plaster of Paris, tech ....bbl.	3.30	3.30	3.30
Potassium Bichromate.......lb.	.10	.09¾	.10
Bromide, imported......lb.	.16	*.16	.14½
Carbonate, calc.,80–85%.lb.	*.06½	*.06½	*.05½
Chlorate, cryst..........lb.	*.07½	*.07½	*.05½
Hydroxide, 88–92%.....lb.	*.07¼	*.07¼	*.08
Iodide, bulk, U. S. P.....lb.	3.75	3.75	3.60
Nitrate................lb.	.06½	.06½	.06½
Permanganate, U. S. P...lb.	*.18	*.17½	*.16
Prussiate, red..........lb.	*.60	*.60	*.90
Yellow.............lb.	*.32	*.32	*.38
Salt Cake, bulk............ton	24.00	24.00	28.00
Silver Nitrate...............oz.	.44	.44	.44
Soda Ash, 58%, bags....100 lbs.	*2.00	*2.00	*2.00
Caustic, 76%, N. Y. 100 lbs.	3.70	3.70	3.50

* Resale or Imported (not an American maker's price).

	Sept. 1	Sept. 15	Jan. 1923
Sodium Acetate.............lb.	.05	.05	.07¼
Bicarbonate....... 100 lbs.	2.25	2.25	2.00
Bichromate.............lb.	.08	.08	.07¾
Bisulfite, powd.........lb.	.04	.04	.04
Chlorate................lb.	.06½	.06½	.06½
Cyanide, 96–98%.......lb.	.23	.23	.23
Fluoride, tech..........lb.	.09½	.09½	.09½
Hyposulfite, bbls... 100 lbs.	2.90	2.90	3.60
Nitrate, 95%...... 100 lbs.	2.42½	2.45	2.57½
Nitrite.................lb.	.07¼	.07¼	.08½
Prussiate, yellow........lb.	.14	.14	.18½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40° ....100 lbs.	.80	.80	.80
Sulfide, 60%, fused......lb.	.04½	.04½	.05
Strontium Nitrate..........lb.	*.10	*.10	*.08¾
Sulfur, flowers.........100 lbs.	3.00	3.00	3.00
Crude, mines......long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n....lb.	.12½	.12½	.10¼
Oxide..................lb.	.45	.45	.43
Zinc Chloride, U. S. P........lb.	.25	.25	.20
Oxide, bbls.............lb.	.08½	.08½	.07½

ORGANIC CHEMICALS

	Sept. 1	Sept. 15	Jan. 1923
Acetanilide, U. S. P., bbls....lb.	.35	.32	.35
Acid, Acetic, 28 p. c.... 100 lbs.	3.38	3.38	3.17½
Glacial ....100 lbs.	12.78	12.78	12.05
Benzoic, U. S. P.........lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drums.............lb.	.30	.30	.32
50- to 110-lb. tins...lb.	.32	.32	.34
Citric, crystals, kegs.....lb.	*.50	*.50	*.48½
Oxalic, cryst., bbls., wks.lb.	.12	.12	.13½
Pyrogallic, resublimed...lb.	1.55	1.55	1.55
Salicylic, U. S. P.........lb.	.35	.35	.45
Tannic, U. S. P., bbls....lb.	.83	.83	.70
Tartaric, cryst., U. S. P...lb.	*.34	*.34	*.32
Acetone, drums.............lb.	.25	.25	.21
Alcohol, denatured, complete. gal.	.46	.46	.45
Ethyl, 190 proof, bbls...gal.	4.75	4.75	4.70
Amyl Acetate.............. gal.	4.50	4.50	2.50
Camphor, Jap, refined, cases .lb.	.93	.93	.86
Carbon Bisulfide, c/1........lb.	.06¾	.06¾	.06¾
Tetrachloride...........lb.	.10½	.10½	.10½
Chloroform, U. S. P., drums..lb.	.35	.35	.35
Creosote, U. S. P............lb.	.50	.50	.40
Cresol, U. S. P...............lb.	.36	.36	.25
Dextrin, corn ....100 lbs.	3.65	3.65	3.09
Imported Potato........lb.	.07	.07	.09
Ether, U. S. P., 100 lbs.......lb.	.13	.13	.13
Formaldehyde, bbls..........lb.	.13	.13	.16
Glycerol, dynamite, drums...lb.	.16	.16	.16½
Methanol, pure, drums......gal.	1.10	1.10	1.35
Methylene Blue, med........lb.	2.25	2.25	2.25
Petrolatum, light amber......lb.	.04½	.04½	.03¾
Pyridine ....gal.	4.00	4.25	2.75
Starch, corn, pow'd.....100 lbs.	3.22	3.22	2.47
Potato, Jap.............lb.	.05	.05	.06¾
Sago...................lb.	.04½	.04½	.03½



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Sept. 1	Sept. 15	Jan. 1923
Beeswax, pure, white.........lb.	.37	.37	.36
Castor Oil, No. 3.............lb.	.13½	.13	.13
Ceresin, yellow...............lb.	.08	.08	.08½
Corn Oil, crude, tanks, mills...lb.	.09	.10	.09¾
Cottonseed Oil, crude, f. o. b. mill.....................lb.	.10	.10	.09⅝
Linseed Oil, raw, lc/l........gal.	.90	.90	.87
Menhaden Oil, crude, mills...gal.	.40	.12½	.53
Neat's-foot Oil, 20°..........lb.	.15	.16½	.18½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	5.90	5.95	6.25
Rosin Oil, first run..........gal.	.45	.45	.45
Shellac, T. N.................lb.	.57	.57	.80
Sperm Oil, bleached winter, 38°....................gal.	.99	.99	1.03
Stearic Acid, double pressed...lb.	.13½	.13½	.12½
Tallow Oil, acidless...........lb.	.09	.10½	.11½
Turpentine, spirits of........gal.	.95	1.02	1.56

METALS

	Sept. 1	Sept. 15	Jan. 1923
Aluminium, No 1, ingots.....lb.	.25	.25	.23
Antimony, ordinary......100 lbs.	6.75	6.75	6.75
Bismuth.....................lb.	2.75	2.75	2.75
Copper, electrolytic..........lb.	.13⅝	.13⅞	.14¾
Lake...................lb.	.13⅞	13⅞	.14¾
Lead, N. Y..............100 lbs.	6.75	6.75	7.80
Nickel, electrolytic...........lb.	.29	29	.36
Platinum, refined, soft........oz.	116.00	116.00	118.00
Quicksilver, flask......75 lbs. ea.	62.00	62.00	73.00
Silver, foreign................oz.	.62⅝	.62⅝	.63
Tin.........................lb.	.40½	.42	.39
Tungsten Wolframite....per unit	8.50	8.50	7.50
Zinc, N. Y..............100 lbs.	6.75	6.85	8.25

FERTILIZER MATERIALS

	Sept. 1	Sept. 15	Jan. 1923
Ammonium Sulfate, expt.100 lbs.	3.45	3.45	3.90
Blood, dried, f. o. b. N. Y...unit	3.75	3.75	4.70
Bone, 3 and 50, ground, raw..ton	25.00	25.00	28.00
Calcium Cyanamide, unit of ammonia	2.25	2.25	2.25
Fish Scrap, dried, wks.......unit	3.80	3.80	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.25	3.25	3.00
Florida, 70%...........ton	3.55	3.55	3.55
Florida, 74–75%........ton	4.50	4.50	4.50
Tennessee, 72%.........ton	5.50	5.50	5.25
Potassium Muriate, 80%....unit	.68	.68	.68
Tankage, high-grade, f. o. b. Chicago...............unit	3.60 & .10	3.60 & .10	4.75 & .10

COAL-TAR CHEMICALS

Crudes

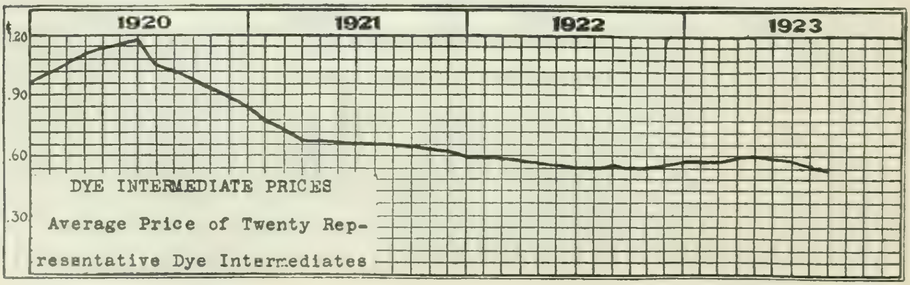
	Sept. 1	Sept. 15	Jan. 1923
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.24	.24	.30
Naphthalene, flake...........lb.	.07	.07	.06½
Phenol, drums...............lb.	.30	.30	.32

Crudes *(concluded)*

	Sept. 1	Sept. 15	Jan. 1923
Toluene, pure, tanks.........gal.	.28	.28	.30
Xylene, 2 deg. dist. range, drums.................gal.	.65	.65	—

Intermediates

	Sept. 1	Sept. 15	Jan. 1923
Acids:			
Anthranilic..............lb.	.96	.96	1.10
Benzoic, tech............lb.	.70	.70	.65
Cleve's..................lb.	1.00	1.00	1.25
Gamma...................lb.	1.70	1.70	1.85
H.......................lb.	.75	.75	.80
Metanilic...............lb.	.60	.60	.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.62	.62	.60
Nevile & Winther's.......lb.	1.10	1.10	1.15
Picric...................lb	.25	.25	.20
Sulfanilic................lb.	.20	.20	.19
Tobias'..................lb	1.30	1.30	1.30
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil..................lb.	.16½	.16½	.17
Aniline Salt.................lb.	.24	.24	.25
Anthraquinone (sublimed).....lb.	1.30	1.30	1.30
Benzaldehyde, tech..........lb.	.75	.75	.65
U. S. P.................lb.	1.50	1.50	1.40
Benzidine Base..............lb.	.82	.82	.84
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol...............lb.	3.80	3.80	3.75
Dianisidine..................lb.	4.60	4.60	4.50
p-Dichlorobenzene...........lb.	.17	.17	.17
Diethylaniline...............lb.	.60	.60	.60
Dimethylaniline..............lb.	.41	.41	.41
Dinitrobenzene...............lb.	.19	.19	.19
Dinitrotoluene...............lb.	.19	.19	.20
Diphenylamine...............lb.	.48	.48	.50
G Salt......................lb.	.55	.55	.60
Hydroquinol.................lb.	1.25	1.40	1.05
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.22	.22	.26
a-Naphthylamine............lb.	.35	.35	.29
b-Naphthylamine............lb.	.75	.75	.95
m-Nitroaniline..............lb.	.78	.78	.80
p-Nitroaniline..............lb.	.74	.74	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol...............lb.	1.00	1.00	.72
o-Nitrotoluene..............lb.	.10	.10	.10
p-Nitrotoluene..............lb.	.60	.60	.65
m-Phenylenediamine.........lb.	.98	.98	1.00
p-Phenylenediamine..........lb.	1.45	1.45	1.50
Phthalic Anhydride..........lb.	.30	.30	.35
R Salt......................lb.	.55	.55	.55
Resorcinol, tech.............lb.	1.40	1.40	1.50
U. S. P.................lb.	2.00	2.00	2.00
Schaeffer's Salt.............lb.	.60	.60	.60
Sodium Naphthionate........lb.	.62	.62	.62
Thiocarbanilide.............lb.	.35	.28	.35
Tolidine (base)..............lb.	.95	.95	.95
Toluidine, mixed............lb.	.31	.31	.30
o-Toluidine.................lb.	.18	18	.15
p-Toluidine.................lb.	.90	.90	1.00
m-Toluylenediamine.........lb.	.90	.90	.95
Xylidine....................lb.	50	.50	.42



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EDITORIALS

The Washington Meeting

THE date of the Washington meeting of the AMERICAN CHEMICAL SOCIETY has been set for the week beginning Monday, April 21, 1924, with hotel headquarters at the New Willard. The local section has been fortunate in securing the Central High School, which is sufficiently large to accommodate all divisions and sections, as the meeting place.

Local sections which have long desired to have one of the semiannual meetings of the SOCIETY in their city, but have been deterred from extending an invitation largely because of the expense involved, will be sure to look with favor upon the innovation which the Washington Section has voted to attempt. The spring meeting will be financed wholly within the chemical profession. Industries and interested friends will not be solicited for contributions, but those attending the meeting will be offered entertainment which, it is thought, will be adequate, and the registration fee will be set at a figure to cover the expense involved. The members of the local section hope to demonstrate that a successful meeting of the SOCIETY can be held without great financial outlay on the part of the local section, and to establish a precedent for other sections to follow in entertaining the SOCIETY in future.

Another innovation will be that on the days following the general meeting and symposia on Tuesday the divisions and sections will meet in the mornings only, leaving the afternoon of each day for excursions, both scientific and popular, for small group meetings, and for relaxation from close attention upon scientific programs.

It is none too early to begin to plan to attend the Washington meeting. The time set for the convention is one of the most delightful seasons of the year, and Washington, always popular with sightseers, is unusually attractive at this particular season of the year. Washington has splendid hotel facilities, but they will be taxed to the utmost during the Easter holidays, and in order to secure the best and most satisfactory accommodations we urge members to make their hotel reservations now. If you desire, H. C. Fuller, chairman of the Committee on Hotels and Transportation, Institute of Industrial Research, Washington, D. C., will make reservations for you. In the near future the announcement of other committeemen will be made, in order that members may make all arrangements directly with the appropriate committees.

Japan

WE DO not know as yet to what extent the chemists and the chemical industry of Japan may have suffered from the earthquake, flood, and fire, but we want our many readers in that country to know that their misfortune has been very much upon our minds and that we have hoped from day to day to receive more definite information. We have been unable to obtain word from our Japanese correspondent since the catastrophe, but hope that our failure to hear does not indicate disaster. Notwithstanding a number of natural handicaps, Japan has made great progress in the chemical industry and we sincerely trust that the gains made at such great cost of time and labor have not been wholly lost.

Alcohol, the Chemical

JUST a year ago we made suggestions in an editorial looking to an improvement in the administration of the National Prohibition Act, so far as it concerns high-proof alcohol used for nonbeverage purposes. In the interim the Commissioner of Internal Revenue has taken a progressive step in organizing an Alcohol Trades Advisory Committee composed of men representing associations of alcohol-using industries, and the AMERICAN CHEMICAL SOCIETY has representation upon this committee. The appointment of the committee and the whole-hearted manner in which the Commissioner of Internal Revenue and the officials of the Prohibition Unit have sought the advice of the group are most encouraging. Officials who have been more concerned with the prohibitory than with the permissive phases of alcohol legislation are beginning to realize that there is such a thing as alcohol, the chemical, and that in prohibiting the use of intoxicating beverages it is necessary to do so without arresting the development of uses of alcohol, the chemical raw material.

A statement has recently been issued by the Alcohol Trades Advisory Committee outlining the present situation and including an appendix in which are listed about five pages of lawful uses of alcohol, pure and denatured, and a chart showing some of the many uses of ethyl alcohol. The distribution of this statement will, it is believed, do much to make available information which, while common knowledge to the scientist, is a revelation to the average Government official and law-maker. The statement contains the following recommendations:

I—As alcohol is admittedly a basic chemical essential to our national defense, industrial and economic development, and even to the advancement of civilization itself, all who believe in true law enforcement should recognize the insufferable situation to which chemical industry has been brought by failure heretofore properly to enforce the industrial alcohol features of the National Prohibition Act, and should make certain that it is administered as intended by Congress.

II—The Alcohol Trades Advisory Committee believes that the action of a former Commissioner of Internal Revenue in vesting in a Federal Prohibition Commissioner, not equipped with the essential technical and economic knowledge and training, the duties of carrying out the provisions of the National Prohibition Act, concerning the manufacture, transportation, sale, and use of industrial alcohol, was illegal by implication, illogical by any method of sound reasoning, economically impracticable, and should be forthwith corrected.

The Commissioner of Internal Revenue should designate a Deputy Commissioner of Internal Revenue, or appoint an Industrial Alcohol Commissioner, to take over the administration of that portion of the law relating to the manufacture, sale, and use of high-proof alcohol, pure and denatured for nonbeverage uses. Collectors of Internal Revenue and Civil Service revenue officers should be selected to assist him, as is customary in the enforcement of other internal revenue statutes. It follows that such a Deputy or Industrial Alcohol Commissioner should possess suitable technical knowledge, training, and experience. It should be his duty to issue permits to manufacture, withdraw, and use industrial alcohol of any kind, a copy of each permit at the time of issuance to be delivered to the Prohibition Commissioner so that he might police operations. In this way, efficient and scientific administration would be assured and at the same time the Prohibition Commissioner would be relieved from routine work incidental to serving legitimate industry, and could devote the necessary time to his logical duty of enforcing the *prohibitory* features of the law. Furthermore, the two agencies, coördinating, would be a check upon each other. *It would not require any change whatsoever in the* *law, but merely a revision of Regulations 60 and 61, to carry this recommendation into effect.*

III—If agreeable to the Commissioner of Internal Revenue, this Alcohol Trades Advisory Committee will act in an advisory capacity for the purpose of assisting such Deputy Commissioner of Internal Revenue or Industrial Alcohol Commissioner in investigating applications for permits and furthering the uses of alcohol in scientific research and lawful industry.

Secretaries of the local sections have been sent copies of the entire statement. This subject should be discussed before local sections and every effort made to have the public gain a better understanding of all that is involved in the use of alcohol for nonbeverage purposes.

Standards and the Metric System

UNDER the progressive leadership of the Department of Commerce much has been accomplished in simplified practice and standardization with the task but just begun. Needless sizes and styles are being eliminated in various lines. Dimensions are being standardized and ultimately the benefit will be derived in the more efficient use of raw material and the lowering of costs, not only in manufacture, but in stocks and turnover.

This is all commendable and we have heartily supported the department's program. We sincerely hope that when this project has fully established itself with manufacturers, jobbers, dealers, and the public, a real simplification and standardization may take place by first abandoning the fallacy of whole numbers in dimensions, and then simplifying our systems of weights and measures. This inevitably means the adoption of the metric system. We do a great deal of thinking and hard work to gain an export market, and with the metric system obligatory in thirty-four countries and optional in eleven more, it is easy to see that, with the notable exception of Great Britain, real effort to do business abroad means the use of the metric system in catalogs, in packages, and in dimensions. Will the American manufacturer be content to carry packages in two systems upon his shelves? Can he afford to do so?

We are confident that much of our difficulty comes through the adhesion to whole numbers or major fractions in the dimensions of materials, with a consequent lack of efficiency. Is it not true that in the design of most manufactured articles a definite size is first chosen because it looks about right and then decided arbitrarily without respect to the size, thickness, or strength which it should have from the standpoint of utility and performance of a definite piece of work? Sometime dimensions will be determined with respect to satisfying rigid laboratory tests, just as materials are tested at present. Dimensions will then require expression in the convenient metric units and mechanics who now are indifferent to the metric system will insist upon its use.

Efficient standardization follows initial diversity for, from a variety, the survival of the fittest brings forth the designs best adapted to service. Automobile experience is an example. From the great variety of cars designed we find some disappearing because they are unsatisfactory, others finding their special place and developing it, and still others produced in quantity and becoming standard because of the service they perform. The standards of today, therefore, may not be expected to serve as the standards for tomorrow, and with the oncoming generation learning to use the metric system in the radio, in the laboratory, and in other directions, may we not soon base our simplified practice and our standardization upon the only system that is international in the broadest sense, cast aside confusion due to the many systems we now endeavor to handle, and concentrate upon the education of the people at large to the appreciation and use of metric units?

Recognition of Scientists

L. H. BAEKELAND, just returned from an extensive trip with renewed appreciation for the opportunities and privileges of the United States, recently brought to our attention the desirability of having Congress recognize in some specific and definite way the triumphs of our men of science, particularly those in department circles. Then in the editorial section of the *New York World* for September 2, Ellwood Hendrick discussed the same sentiments and made a plea for such recognition by Congress. We wish to add our voice and urge that something be done in a proper way to have our law-makers realize that "the United States is the only civilized country in the world that does not recognize distinguished service by civilians. In the British Empire they make them lords or knights—and we cannot do that. In France, Italy, Spain, Belgium, Portugal, China, Japan, and even in Soviet Russia, they give decorations. We do not give decorations to civilians. Moreover, the insignia of decorations have been preëmpted by so many private organizations in this country that a button in the lapel of a man's coat is without its significance elsewhere."

But there are other ways in which this Nation can express its thanks. Perhaps some day we may go as far as our neighbor Canada and grant a substantial annuity to a man who has made a scientific discovery of great importance to the public. There seems no reason why Congress could not pass an act, engrossed and signed by the President of the United States, consisting of a proper preamble and resolution commending and expressing gratitude to a man who has devoted many years of his life, his ability as a scientist and perhaps as an inventor, to the welfare of the republic.

Such a document would be invaluable to the recipient. Moreover, the adoption of a policy of this kind might be the first step in working out a really adequate plan for rewarding scientists, many of whom have steadfastly refused more remunerative offers out of pure patriotism. Such action might be taken only upon the retirement of a departmental head or bureau chief, but those are details. The point we want to make now is that the devotion and sacrifice of our chemists to the science should be recognized in some way.

Electrical Wars

THE efforts of some misinformed enthusiasts to discredit chemical warfare have been of small avail, thanks to the readiness with which the American people have grasped the truth. Perhaps those who oppose the application of the science, chemistry, to defense would also limit research in electricity because of the prediction made by Professor Low of London. He suggests the possibility of using jets of electrically charged water to kill horses and men; calls attention to the efficiency of wireless control of tanks and airplanes; of wireless telephony, sight, heat, and power; of battleplane engines developing wireless power to destroy aircraft within a wide radius; of the possibility of conducting propaganda striking terror into the home by means of wireless receivers; of airplanes with electric impulse by which guns could be fired at an enormous rate; of electrically controlled rockets operated on wires for wrecking planes; and, of course, the wireless-controlled torpedo with a wireless sighted periscope controlled by a secret combination of wave lengths. Perhaps we may have controllable lightning and monsters of the air and sea, the progenitors of which are already an actuality.

However much we should like to see the coming of the millennium, there is so far nothing to justify relaxation in research in any of the sciences, and least of all in chemistry.

Institute of American Meat Packers

AMONG the associations of industrialists engaged in scientific research, none deserves more encouragement than the Institute of American Meat Packers. Making progress cautiously, the institute has nevertheless accomplished much through its Committee on Scientific Research, and the vista of the future is most encouraging.

Arthur Lowenstein, vice president of Wilson & Company, has established a substantial fellowship on the prevention of meat spoilage, and the institute has sanctioned a research fellowship at Mellon Institute on the utilization of by-products. A series of lectures under the joint auspices of the School of Commerce and Administration of the University of Chicago and the institute has been inaugurated, and courses of instruction have been arranged so that the employees in the packing plants will have a better opportunity to fit themselves for their work. The courses are intended primarily for those now occupying minor executive positions and who are ambitious to become executives. Both day courses for full-time study and evening courses are announced. This experiment will be watched with great interest. Correspondence work will begin later in the academic year and research to extend the boundaries of scientific knowledge will be undertaken soon.

Concurrently, the Committee on Scientific Research of the institute is developing plans for extensive work under the direction of its own staff, and has in view such important investigations as a study of a substitute for sugar in meat curing. Coöperation is being sought with trade organizations, Government bureaus, and others having a mutual interest in the problems of the packing industry, and following a scientific survey of the industry we may expect an announcement of an extensive and detailed program.

The packing industry has always been known for its achievements in applied science and the prosecution of fundamental research. This work has been done in the individual plants and laboratories. The coöperative research of the institute can be carried to success without detracting from the importance of these individual laboratories. There are sufficient fundamental problems to engage the thought and energy of all concerned.

Trade Secrecy

A PRESS dispatch dated London, October 17, states:

> A secret formula for making dye by a method said to require only a fraction of the usual cost has been carried to the grave by a London pauper, Robert Culver, who learned from a German relative years ago and brought it to England, where he organized a dye manufacturing company.
>
> The concern, however, failed through dishonesty of some of its officials and Culver was reduced to poverty. He died recently in a poorhouse without telling any one of the process.

We know nothing of the value of the secret in question, but we desire to emphasize again that secrecy in industrial processes and in scientific work belongs in the past and has little part in modern affairs. There are still those who jealously guard all the minute details of any formula or process, but they are outnumbered by those who know that in skill and technic there lies the protection which justifies them in discussing in some detail the various steps in a particular formula. As one such expressed himself, "My formula is as open as a violin. There it is. Now play it." Our own experience with certain much-discussed formulas and patents indicates that those with training and a deep interest can learn to play and that in a frank discussion of processes those who give always profit directly by the exchange of ideas.

Making the Chemical Show Chemical

CRITICISM of the Ninth National Exposition of Chemical Industries has taken much the same form and come from much the same sources as that of its predecessors—"Chemical industries were sadly lacking although everyone with something to sell that industry was represented. The show has become more and more an equipment show and not a chemical one." This type of criticism may be justified, but hardly can it be when unaccompanied by suggestions of ways and means to overcome the trouble.

Let us look for a moment at the reasons for the absence of strictly chemical manufacturers from such a gathering. The most natural and perhaps the most important reason for this apparent defection of the key section of the exposition has been that chemical manufacturers have failed to get monetary returns for their expenditures on exhibits. Quite naturally altruism is no more a part of the scheme of the chemical manufacturer than it is of any other, so that it is necessary to take this point into serious consideration. The equipment manufacturers have found the exposition profitable and hence have continued to exhibit. They have taken advantage of one very definite point in preparing their exhibits which the chemical group apparently failed to consider. *New* equipment and *new* wrinkles in old equipment are shown alongside the same old bottles, kegs, and barrels of chemicals which present nothing in the least new. In this lies the secret of the success of the one and the failure of the other.

Visitors to recent shows will recall the long decorative hangings of crystals of copper sulfate in the booth of one chemical manufacturer, for example, which were truly beautiful. But what did they mean to the chemical consumer? Nothing! He was not interested in the least in buying copper sulfate for decorating either his home or his plant. He was interested, let us say, in its use in preparing a new insecticide, but he was shown a decoration. The attention value of such decorations in coaxing visitors to pass near a booth is great, but their value in getting visitors into the booth to buy is an altogether different matter. To continue the case, let us suppose that within the booth were examples of some entirely new and strange use of copper sulfate, such as in the curing of human hair for hair nets, or the fireproofing of theatrical hangings, if either were possible. Properly displayed, such processes would coax in interested visitors far more readily than the simple exhibit of a few bottles and kegs of well-known products of this material.

Here, then, is the germ of the idea which will bring interested buyers to the point of at least leaving their names, if not actually signing on the dotted line—*get their interest by something new.* We think of many new developments which could have been shown to advantage, and as proof of our contention we cite the exhibit of the American dye industry and that of the AMERICAN CHEMICAL SOCIETY, both of which presented old ideas in entirely new ways, so far as the exposition was concerned. True, neither of these booths was designed to *sell* definite products, but it is equally true that these two booths competed with endless exhibits of machinery in motion, and most successfully. The chemical manufacturers can do the same if they will only confine their efforts to new ideas or new ways of presenting old ones, instead of endless arrays of specimens of products with which the entire chemical world is perfectly familiar. The whole scheme of the exposition cannot be justly criticized for the failure of exhibitors to take full advantage of their opportunities.

Some Factors Influencing the Design of Absorption Apparatus[1]

By R. T. Haslam, W. P. Ryan, and H. C. Weber

Massachusetts Institute of Technology, Cambridge, Mass.

The advisability of studying absorption by methods successfully used in the study of the similar and related field, flow of heat, is pointed out.

The effect of the two resistances, the "gas film" and the "liquid film," is shown by studying the effect of gas velocity or the absorption of sulfur dioxide by water. The gas-film resistance appears to be proportional to the gas velocity to the 0.8 power. The liquid-film resistance appears to be practically independent of the gas velocity. The over-all coefficient of absorption rises rapidly with an increase in gas velocity reaching an asymptote due to the comparatively stationary liquid-film resistance.

The equations connecting the rate of absorption with gas velocity are given.

IN THE design of an absorption system we are usually concerned with the size of tower or scrubber necessary to absorb a given amount of material per hour under fixed terminal conditions—e. g., concentration of entering gas, temperature of scrubbing liquid, per cent recovery, etc. Oftentimes, in addition, it is desirable to know how a change in one or more of these terminal conditions will affect either the size unit required, the capacity of a given unit, or the per cent of material lost in the exit gases. Both problems involve the rate at which matter is transferred from a gas to a liquid or vice versa. Here, as in the cases of the flow of electricity and the flow of heat, the rate of transfer is proportional to a "driving force." In the flow of heat this driving force is the temperature difference between the hot and the cold body; in electricity the driving force is the potential difference or e. m. f. existing between the two points; in absorption it is the distance the gas-liquid system is from equilibrium. In the case of the flow of electricity the resistance also influences the quantity of electricity that will flow in a given time. With the transfer of heat the same situation holds true—the amount of heat that flows from a hot body to a cold one in a unit time is not only proportional to the temperature difference (driving force), but it is also inversely proportional to the resistance through which the heat must flow. So, too, with the transfer of material in absorption apparatus, the rate of flow of the material from one phase to the other is not only proportional to the driving force (distance the system is from equilibrium), but it is also inversely proportional to the resistances in between the gas and liquid—namely, as shown by Whitman and Keats,[2] the gas film and the liquid film. These film resistances are not due to actual stationary films through which heat flows by conduction and material by diffusion, but in both cases at present these resistances are considered as equivalent to stationary films of varying thickness.

The similarity between the flow of heat and the transfer of material from a gas to a liquid phase, or vice versa, does not end with the fact that each is proportional to a driving force and inversely proportional to a resistance. It has been shown also that the major resistances in both cases are equivalent to film resistances, gas and liquid films, and, in addition, W. K. Lewis[3] has shown that under certain limiting conditions the coefficient of material transfer is proportional to the coefficient of heat transfer. In view of this similarity it seems advisable to study the rate of absorption (or transfer of material from gas to liquid) in a manner similar to the study of the older science, the flow of heat. Newton's law on the flow of heat is as follows:

$$\frac{dQ}{d\Theta} = \left(\frac{hA}{dl}\right) dt \qquad (1)$$

where $dQ/d\Theta$ is the quantity of heat flowing per unit of time through the area A of thickness, dl, when the driving force or temperature difference is dt. The constant h is the coeffi-

---

[1] Received August 27, 1923. Revised from a paper presented at the meeting of the American Institute of Chemical Engineers, Richmond, Va., December 6 to 9, 1922.

[2] This Journal, **14**, 186 (1922).

[3] *Mech. Eng.*, **44**, 445 (1922).

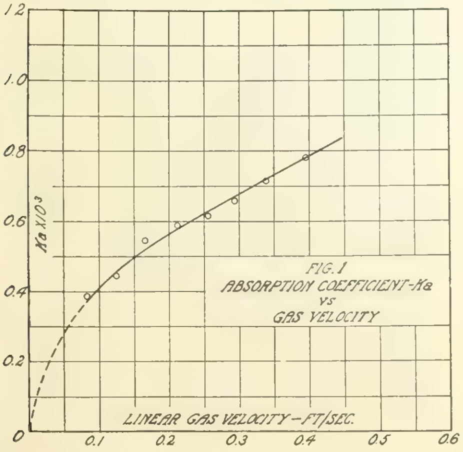

FIG. 1
ABSORPTION COEFFICIENT—Ka
VS
GAS VELOCITY

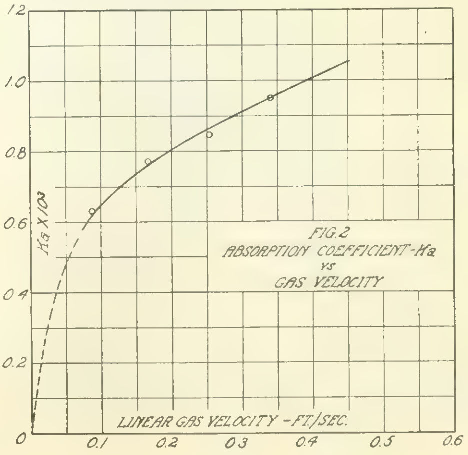

FIG. 2
ABSORPTION COEFFICIENT—Ka
VS
GAS VELOCITY

cient of heat conductivity. This equation has the same form as Ohm's law, where

$$\text{Quantity (current)} = \frac{\text{Driving force (e. m. f.)}}{\text{Resistance}}$$

where $dQ/d\Theta$ is the quantity factor, dt the driving force, and dl/hA is the resistance. In the transfer of heat $1/h$ is the *total* or *over-all* coefficient of resistance, often composed of three resistances, the intervening wall, and the fluid film resistences on either side of the wall. An exact knowledge of the laws governing the flow of heat was brought about, not by investigating the over-all coefficient of resistance, $1/h$, but by determining the coefficients of resistance of the walls and the films separately and noting how such variables as materials, velocity, temperature, etc., changed each resistance. Knowing each of the resistances, one may easily calculate the over-all resistance. In heat transfer the main problem is the determination of the two film coefficients. As shown by Weber[4] the coefficient of heat transfer for *gaseous films* (forced convection) is as follows:

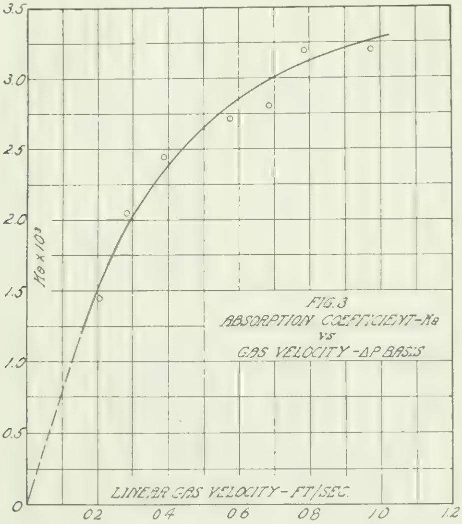
FIG. 3 ABSORPTION COEFFICIENT-Ka vs GAS VELOCITY -ΔP BASIS

$$h_g = \frac{0.88\,(V_m)^{0.8}\,(T)^{0.5}\,(S)^{0.2}\,(C_p)}{M^{0.3}} \qquad (2)$$

where h_g = coefficient of heat transfer through the gaseous film
V_m = the mass velocity of the gas
T = gas temperature in degrees centigrade absolute
S = surface factor $\left(\frac{\text{area}}{\text{volume}}\right)$
C_p = specific heat of gas at constant pressure
M = molecular weight of gas

McAdams and Frost[5] have shown that the coefficient of heat transfer through a *liquid film* is as follows:

$$h_L = \frac{23.3\,K\,(DVz)^{0.8}}{D} \qquad (3)$$

where h_L = coefficient of heat conduction
K = thermal conductivity of stationary liquid
D = diameter of pipe through which liquid flows
z = fluidity of film on pipe relative to water
V = average mass velocity of liquid

From these two equations it is seen that the resistance of the gaseous film, $1/h_g$, is inversely proportional to the gas velocity to the 0.8 power, and that the resistance of the liquid film, $1/h_L$, is inversely proportional to the 0.8 power of the liquid velocity and the 0.8 power of the fluidity.

Turning now to material transfer or absorption, the rate of absorption of one material from a stream by another stream of material flowing countercurrent to the former may be expressed in a manner similar to the flow of heat (Equation 1).

$$\frac{dW}{d\Theta} = ka\ V\ \Delta P \qquad (4)$$

where $\frac{dW}{d\Theta}$ = weight in pounds of material being absorbed per minute
ΔP = driving force or distance from equilibrium, often expressed as pressure difference between the partial pressure of solute in gaseous and liquid phases, expressed in millimeters of mercury
V = total interior volume of apparatus in cubic feet
ka = over-all absorption coefficient equivalent to the pounds of gas absorbed per minute per cubic foot of volume per millimeter mercury partial pressure difference when ΔP and V are expressed as above

This differential may be expressed as an average equation of rate

$$\frac{W}{\Theta} = kaV\,(\Delta P)_{\text{av.}} \qquad (4a)$$

When the gas obeys Henry's law and the temperature effects are small, the $\Delta P_{\text{av.}}$ is the logarithmic mean of the pressure differences between the partial pressure of the solute in the gaseous and liquid phases taken at the ends of the system. In this equation the over-all coefficient of absorption, k, is coupled with the unknown area through which absorption takes place, a. The over-all coefficient, ka, is proportional to $\frac{1}{R_g + R_L}$, where R_g is the resistance of the gas film and R_L is the resistance of the liquid film.

The following experimental work absorbing sulfur dioxide from burner gas by water was carried out with the view of studying the effect of gas velocity and temperature on the rate of absorption, with the hope thereby to obtain more information regarding the nature of the film resistance and to see if the resultant over-all coefficient of absorption, ka, could be explained on the basis of two films, gaseous and liquid, in series each obeying a law similar to that governing the flow of heat through similar films.

EXPERIMENTAL RESULTS

Series I was made with an unpacked tower 8 inches in diameter by 30 inches high, through which water was fed down the inside wall at a rate equivalent to 16.8 pounds per square foot of cross-sectional area per minute at a constant

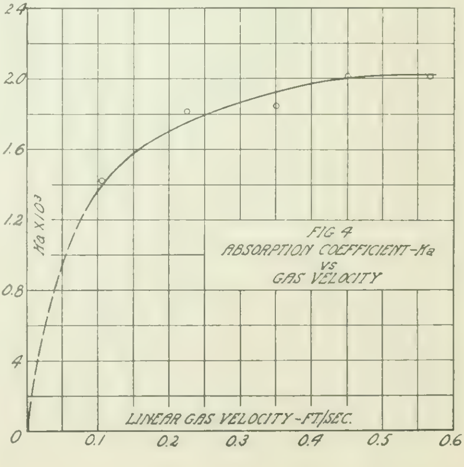
FIG 4 ABSORPTION COEFFICIENT-Ka vs GAS VELOCITY

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[4] M. I. T. Thesis, **1919**.

[5] THIS JOURNAL, **14**, 13, 1101 (1922).

temperature of approximately 58° F. The velocity of the gas was varied from 0.084 foot per second to 0.396 foot per second, and the rates of absorption, absorption coefficient, and per cent absorption are given in Table I. The absorption coefficient is plotted *vs.* gas velocity in Fig. I.

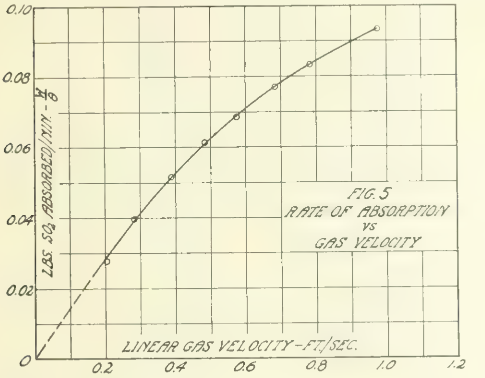

FIG. 5
RATE OF ABSORPTION
VS
GAS VELOCITY

TABLE I—RATE OF ABSORPTION *vs.* GAS VELOCITY

Gas Velocity Ft./Sec.	$ka \times 10^3$	Lbs. SO_2 Absorbed/Min. $\frac{dW}{d\Theta}$	ΔP Mm. Hg	Per cent of Total SO_2 Absorbed
		Series 1		
0.084	0.39	0.0134	39.2	47.3
0.125	0.44	0.0162	42.0	40.5
0.166	0.55	0.0204	42.5	30.0
0.213	0.59	0.0208	40.5	31.6
0.256	0.61	0.0221	41.5	30.0
0.294	0.66	0.0252	43.7	26.0
0.339	0.71	0.0270	43.5	24.5
0.396	0.78	0.0286	42.0	17.0
		Series 2		
0.088	0.63	0.0225	41.1	68
0.167	0.77	0.0304	45.2	49
0.254	0.85	0.0382	51.5	34
0.341	0.95	0.0438	52.8	30

Series 2 was made in the same tower as Series 1, but the water was sprayed in at the rate of 32.6 pounds per square foot of cross section per minute. The temperatures were approximately constant at 55° F. The gas velocity was varied from 0.088 foot per second to 0.341 foot per second. The resultant data similar to that taken in Series 1 are shown in Table I, and in Fig. 2 *ka* is plotted against gas velocity.

Series 3 was made with the same tower packed with 1-inch diameter coke, the water rate being 32.3 pounds per square foot of cross section per minute and the temperature approximately 56° F. The gas velocity was varied from 0.204 to 0.976 foot per second and the results are shown in Table III and in Fig. 3 the absorption coefficient, *ka*, is plotted against gas velocity.

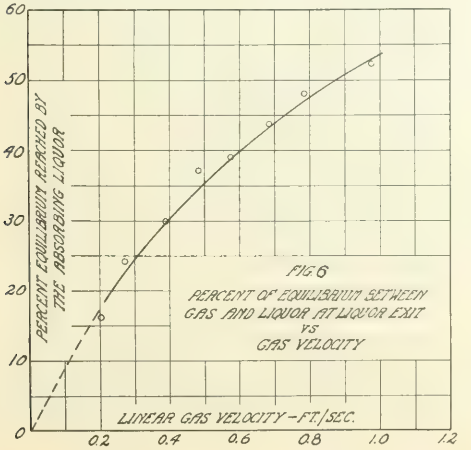

FIG. 6
PERCENT OF EQUILIBRIUM BETWEEN GAS AND LIQUOR AT LIQUOR EXIT
VS
GAS VELOCITY

TABLE II—EFFECT OF LINEAR GAS VELOCITY ON ABSORPTION

Gas Velocity Ft./Sec.	$ka \times 10^3$	Lbs. of SO_2 Absorbed/Min. $\frac{dW}{d\Theta}$	ΔP Mm. Hg	Per cent SO_2 Absorbed	Per cent Equilibrium Reached
		Series 3			
0.204	1.46	0.0278	21.8	40.1	16.2
0.282	2.06	0.0398	22.2	41.2	24.3
0.389	2.45	0.0516	24.0	39.1	30.0
0.484	2.71	0.0614	26.2	39.2	37.2
0.578	2.72	0.0686	29.1	34.1	39.0
0.684	2.79	0.0770	31.4	32.4	43.8
0.785	3.17	0.0833	30.1	31.6	48.3
0.976	3.18	0.0933	33.2	26.7	52.8
		Series 4			
0.113	1.41	0.0256	20.8	92.0	15.8
0.223	1.81	0.0480	30.3	77.7	28.4
0.352	1.84	0.0627	39.0	61.1	35.0
0.449	2.06	0.0688	38.1	50.5	40.5
0.565	2.02	0.0694	39.4	47.7	40.2

Series 4 was made with a tower 8 inches in diameter, 30 inches high, packed with 3 x 3-inch spiral tile, the water rate being 32.1 and the temperature approximately 60° F. The gas velocity was varied from 0.1 foot per second to 0.565 foot per second. The results are given in Table II, and in Fig. 4 the absorption coefficient, *ka*, is plotted against gas velocity.

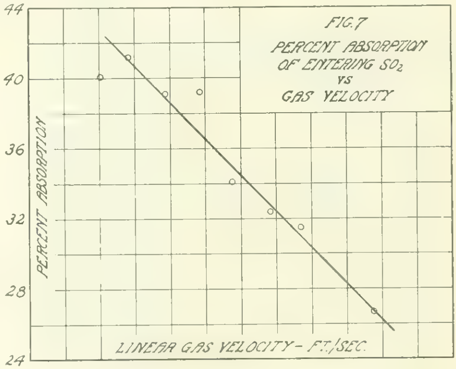

FIG. 7
PERCENT ABSORPTION OF ENTERING SO_2
VS
GAS VELOCITY

DISCUSSION OF RESULTS

EFFECT OF GAS VELOCITY—In all cases (Series 1 to 4 and Figs. 1 to 4, inclusive) it will be seen that with an increase in gas velocity *ka* increases probably from zero (or a point near to it) at a rapid rate, the increase in *ka* growing less at the high gas velocities. Fig. 5 shows how the rate of absorption (pounds sulfur dioxide absorbed per minute, Series III) increases with gas velocity. This also is indicated in Fig. 6, which shows how the per cent equilibrium reached by the absorbing liquor increased from 15 to 52 per cent with an increase in gas velocity from 0.2 per second to 1.0 foot per second. However, the exit losses increase with gas velocity, as shown in Fig. 7, which gives the per cent absorbed *vs.* gas velocity.

In considering Equation 2 for the transfer of heat through gas films, it is seen that increased gas velocity increases the heat transfer through the gas film proportional to the mass velocity of the gas to the 0.8 power, or, in other words, the *resistance* to the flow of heat decreases *inversely* as the velocity to the 0.8 power. Now if the resistance $1/ka$ to the transfer of sulfur dioxide from the gas to the liquid is composed of a gas film and a liquid film, then

$$\frac{1}{ka} = R_g + R_L$$

Assuming that the gas resistance varies inversely as the gas velocity and that gas velocity has no effect on the liquid film, we have

$$\frac{1}{ka} = \frac{C}{V^{0.8}} + R_L \qquad (5)$$

ka = absorption coefficient C = constant
V = gas velocity R_g = gas-film resistance
R_L = liquid-film resistance

Whitman and Keats[2] do not consider the liquid film to be unaffected by gas velocity, while Robinson[6] finds otherwise. Fig. 8 shows $1/ka$ plotted against $1/V^{0.8}$ for Series 1 to 4, inclusive, the points falling close to straight lines as one would expect if Equation 5 is correct. Based on these assumptions, the relative liquid-film resistance and the gas-film resistance at different velocities were computed and the results are shown in Table III.

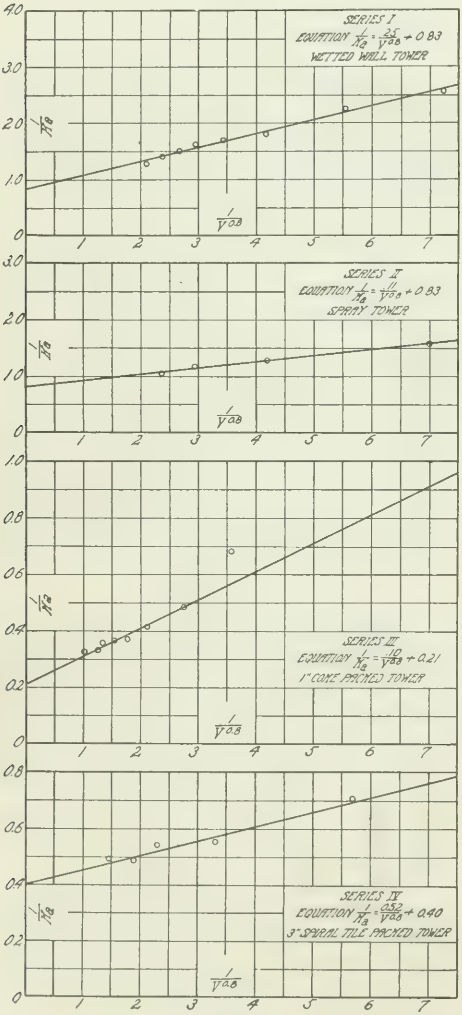

FIG. 8

TABLE III—RELATIVE LIQUID AND GAS FILM RESISTANCES AT VARIOUS GAS VELOCITIES

Series	PACKING	Liquid Resistance	Gas Resistance, R_g, at Gas Velocity of: 0.1 Ft./Sec.	0.3 Ft./Sec.	0.5 Ft./Sec.
1	Wall only wetted	0.83	1.57	0.66	0.44
2	Spray	0.83	0.69	0.29	0.19
3	1-in. diameter coke	0.21	0.63	0.26	0.17
4	Spiral tile	0.40	0.33	0.14	0.10

The equations connecting the absorption coefficient, ka, expressed in pounds per minute per cubic foot of volume per millimeter mercury partial pressure difference with gas velocity, V, in feet per second are as follows:

Series	PACKING	EQUATION
1	Wetted wall	$\frac{1}{ka} = \frac{0.25}{V^{0.8}} + 0.83$
2	Spray	$\frac{1}{ka} = \frac{0.11}{V^{0.8}} + 0.83$
3	1-inch coke	$\frac{1}{ka} = \frac{0.10}{V^{0.8}} + 0.21$
4	3-inch spiral tile	$\frac{1}{ka} = \frac{0.052}{V^{0.8}} + 0.40$

The first term on the right-hand side of the equations is the gas resistance term, while the second refers to the water resistance. In Series 2, 3, and 4 the water rate was constant at approximately 32 pounds water per square foot per minute, while in Series 1 it was 17 pounds.

It is to be noted that the liquid-film resistances follow the order of magnitude one would expect—namely, that it is least with the 1-inch coke-packed tower and greater with the spray and wetted-wall type of tower. The spiral-packed tower is intermediate in this respect between spray and the coke-filled towers. From an inspection of Table III and Figs. 1 to 4, inclusive, and Fig. 8, it can be said that the data show the effect of the two films, the effect of gas velocity at low gas velocities being great since the main resistance is the gas film, whereas at high gas velocities the effect is due to the increasing importance of the fairly constant liquid film. Furthermore, these data indicate why increased gas velocity has such a small effect on the absorption coefficient of spray type of towers—namely, that the liquid-film resistance, which is fairly constant with increasing gas velocity, is the major resistance, in addition to the gas resistance being excessively high due to "slippage" between the gas and liquid. This treatment shows quickly the line of attack along which to improve any given type of absorption tower—that is to say, for example, whether the liquid-film resistance should be lowered by increased water velocity or the gas-film resistance lowered by increased air velocity.

It is of importance to note that Robinson[6] finds the absorption coefficient ka of cooling towers to be linearly proportional to the air velocity, the line for ka versus air velocity passing through zero. As pointed out by Robinson[6] and Whitman and Keats,[2] during adiabatic humidification or air cooling the water temperature remains constant, with the result that no liquid film exists, leaving only one film resistance, the gas film. Robinson's[6] data show that the gas-film resistance is inversely proportional to the gas velocity to the 0.8 power, and that the liquid-film resistance, in the case mentioned, is zero.

ACKNOWLEDGMENT

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[6] *Mech. Eng.*, **45**, 99 (1923).

The Standardization of Commercial Viscometers[1]

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The need of the standardization of viscometers, and the advisability of expressing results in absolute units has been discussed.

The calibration, set up, and operation of a typical glass outflow type of viscometer have been given, together with comparisons of various other similar types.

Data showing comparative results of viscosity determinations on the various instruments are given.

A typical calibration of the MacMichael torsional viscometer for a single range of viscosity has been studied and comparative data have been included showing unexplained discrepancies in viscosities of glue solutions determined by this instrument and by instruments of the capillary outflow type.

Liquids and solutions suitable for the standardization of commercial types of viscometers have been briefly discussed.

IN DETERMINATIONS involving viscosity there has been an urgent need for the practical application of existing methods to the standardization of commercial viscometers which are in general use in the present industrial laboratory and for the expression of results in terms which may be checked in other laboratories within a reasonable limit of accuracy. These instruments are generally constructed of glass of varying shapes and dimensions, and the results of tests on them are never strictly comparable, owing to these variations and the impossibility of exactly reproducing the critical dimensions in glass. To be sure, various methods of calibration of most "standard" commercial instruments are now available. We have, then, only to select the method which is most suited to the type of instrument available, and by careful determinations on liquids of known viscosities, covering the range in which the viscometer is to be used, to obtain a calibration curve for that particular instrument. Obviously, this method of calibration is the only one available with instruments of the type where dimensions are not known.

A calibration of this kind serves two definite purposes. In the first place it expresses the results in absolute units, a system which cannot be too highly recommended. The expression of viscosity in arbitrary units, such as seconds of outflow or degrees MacMichael, or in relations such as the ratio of time of outflow to the time of outflow for water, is entirely inadequate and very confusing, especially with instruments of the type described above. Secondly, the results may be duplicated in separate laboratories. Materials which are purchased on viscosity specifications may be accurately defined in this regard. Moreover, in the case of fragile instruments, such as glass, where dimensions cannot be accurately duplicated, it is essential to calibrate in order to duplicate results should the instrument be broken. Such instruments are at present in use in many industrial laboratories. Calibration, then, especially in absolute units, is highly desirable.

The viscometers of the short tube type most widely used for oils are the Saybolt Universal, Saybolt Furol, Engler, Redwood, and Barbey. The Saybolt Universal,[2] Saybolt Furol,[3] Engler,[4] and Redwood[5] instruments have already been standardized as to their principal dimensions, within allowable tolerances, and thus have been made available as standard instruments which when used with the equation for each type express results in the absolute unit of viscosity.

It has been found, however, that with certain classes of tests in industrial laboratories, such as the testing of glues, these standard instruments are not suitable, owing mainly to the fact that the difference in results of tests from the lowest to the highest grades is not great enough clearly to define the many grades which must be designated between them. This so-called "spread" from one grade of glue to the next is especially narrow on the low viscosity glues. For this reason mainly, other instruments of various types, usually of glass and with a much longer capillary (to increase the spread), are commonly employed. It is with the typical calibration of several of these types, together with a typical calibration of the MacMichael torsional viscometer, that this investigation is concerned.

Calibration and Use of a Viscosity Pipet

A type of pipet studied is shown in Fig. 1. It is essentially a 100-cc. pipet bulb with a somewhat larger bore tube and funnel at the top, and a 3-inch glass capillary, inside diameter about 0.25 cm., sealed on the bottom of the bulb. The pipet was immersed in a water jacket consisting of an inverted 5-pound bottle, the bottom of which had been cut off. The bath was heated with a specially designed electrical heating unit controlling accurately the temperature within ± 0.1°C., agitation being effected by means of a slow current of compressed air.

The general method of procedure was to bring the temperature of the liquid to be tested slightly above or below the desired temperature, according to whether the temperature of the determination was above or below that of the room, and after pouring into the pipet to adjust it by means of an accurately graduated thermometer. A slight stirring was effected by moving the thermometer up and down within the pipet. When the desired temperature was reached, the thermometer was withdrawn and the head adjusted to an etched line, *A*, located on the upper tube, and the time

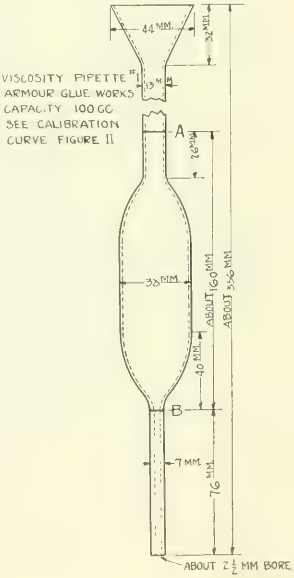

Fig. 1

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[1] Received May 21, 1923.

[2] *Bur. Standards, Tech Paper*, **112** (1919).

[3] *Chem. Met. Eng.*, **26**, 1175 (1922).

[4] *Bur. Standards, Tech. Paper* **100** (1917); **112** (1919).

[5] *Ibid., Tech. Paper* **210** (1922).

measured from this point to another etched line, B, at the top of the capillary tube.

The general equation for viscosity for any given instrument, the critical dimensions of which are unknown and depend on flow due to gravity, is

$$\frac{\mu}{\gamma} = At - \frac{B}{t} \qquad (1)$$

in which μ is the absolute viscosity in centipoises, γ is the density in grams per cubic centimeter, t is the time of outflow in seconds, and A and B are constants of the given instrument. The first term, $\frac{\mu}{\gamma}$, is usually designated as kinematic viscosity—that is, absolute viscosity divided by the density. It has been found that when known kinematic viscosities are plotted against seconds of outflow of these liquids (Fig. 2) a smooth curve results. It will be noted that with this particular type of pipet, as with most other commercial viscometers, the curve bends slightly near the lower end and approaches a straight line at the upper end. This deviation from the straight line is due to the correction for the effect of the kinetic energy, which is the energy required to set the liquid in motion as distinguished from the actual energy required to overcome viscous resistance in the capillary. When equivalent volumes are delivered over variable periods of time, this correction increases as the time of outflow decreases. The third term, $\frac{B}{t}$, of Equation 1 represents this kinetic energy correction. With liquids of high viscosity it becomes negligible and Equation 1 may be written

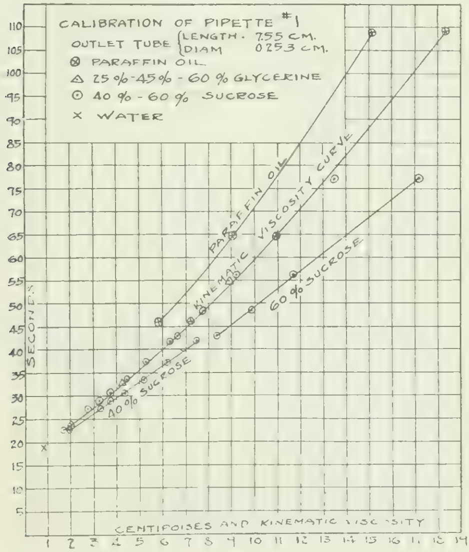

Fig. 2

$$\frac{\mu}{\gamma} = kt \qquad (2)$$

which indicates that kinematic viscosity in these cases is directly proportional to the time. It will be noted also on Fig. 2 that when seconds of outflow of the same liquids at the various temperatures are plotted against the absolute viscosity in centipoises, for each of the three calibrating liquids used three separate and distinct curves are obtained, their positions with respect to the kinematic viscosity curve depending on whether they have a density greater or less than one; but when these values are changed over to the corresponding kinematic viscosities the continuous kinematic curve shown is obtained.

There are several methods[2] of finding the two constants A and B in Equation 1. The method used in the calibration of these pipets consists in finding the time of discharge of two liquids of known widely different viscosities. These values of t, together with the known corresponding values of μ and γ, are then substituted in Equation 1. The two simultaneous equations are then solved for A and B. In order to check the relation between kinematic viscosity and time thus found, several other solutions of intermediate, known viscosities were run and found to check remarkably well with the values calculated. (Fig. 2 and Table I) The liquid of lower viscosity must be so selected that the type of flow is still viscous—that is, in straight-line motion, since the equation does not hold true when the flow is turbulent.

Table I—Viscosities of Solutions Compared with Calculated Viscosities Determined with Pipet 1

(A = 0.1807; B = 54.0)

Temperature ° C.	Seconds	Centipoises	Kinematic Viscosity	Calculated	Error
		Medicinal Paraffin Oil			
30	104.0	15.15	18.27[a]	18.27	0.00
45	64.8	8.96	10.92	10.89	0.03
60	46.2	5.87	7.22	7.18	0.04
		25 Per cent Glycerol			
20	23.9	2.18	2.06[a]	2.06	0.00
		45 Per cent Glycerol			
20	32.8	4.69	4.22	4.27	0.05
		Water			
30	19.2	0.80	0.81	0.66	0.15
		60 Per cent Sucrose			
65	43.0	8.34	6.61	6.52	0.09
60	48.2	9.83	7.77	7.58	0.19
55	56.2	11.67	9.26	9.20	0.06
50	65.0	14.01	11.03	10.89	0.14
45	77.0	17.18	13.49	13.20	0.29
		40 Per cent Sucrose			
60	22.8	1.98	1.71	1.76	0.05
40	27.2	3.25	2.78	2.94	0.16
35	28.8	3.76	3.22	3.33	0.11
30	30.6	4.38	3.74	3.76	0.02
25	33.5	5.19	4.42	4.44	0.02
20	37.2	6.20	5.27	5.27	0.00
15	42.0	7.47	6.34	6.31	0.03
		44.11 Per cent Ethyl Alcohol (by Weight)			
30	24.6	2.02	2.18	2.25	0.07
		60 Per cent Glycerol			
20	55.0	10.31	8.96	8.86	0.10
		Castor Oil			
40	1349.4	231.0	244.0	243.7	0.30

[a] These two values were used in calculating the A and B constants in Equation 1.

To determine the absolute viscosity, then, of any unknown liquid, it is necessary to determine the time of discharge and from a calibration curve or by calculation from the A and B constants in Equation 1 to obtain the kinematic viscosity. This value multiplied by the density at the temperature of the test gives the absolute viscosity in centipoises.

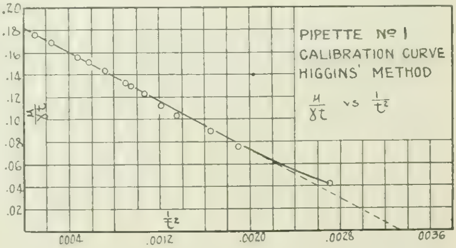

Fig. 3

A graphical method for the determination of the A and B constants in Equation 1 for any given instrument has been evolved by Higgins.[6] He combines Equations 1 and 2

$$k = \frac{\mu}{\gamma t} = A - \frac{B}{t^2}$$

and plots the values $\frac{\mu}{\gamma t}$ against $\frac{1}{t^2}$. The data given in Table I for Pipet 1 were used in plotting these values in Fig. 3. The A factor, then, is numerically equal to the intercept of the line on the axis of ordinates, while the B factor is equal to the tangent of the angle which the straight portion of the line, extended to the axis of abscissas, makes with that axis. This method has the advantage that it aids in selecting a suitable calibrating liquid for the low point on the curve, as it is thereby possible with most types to obtain a series of points near the lower end which will indicate where the straight line begins to break, giving high values for $\frac{\mu}{\gamma t}$ and causing the line to bend upwards. From the value of $\frac{1}{t^2}$, at which this break occurs, may be calculated, approximately, the number of seconds of outflow below which the instrument may not be used and which is near the region of critical velocity—that is, the region of change from viscous to turbulent flow. The position of this region varies with the dimensions of the capillary, but in general the shorter the capillary the lower will be the velocity at which turbulence begins. It is of utmost importance in the calibration of any instrument of this general type to determine, at least approximately, this region of change of flow. It may not be possible to obtain the exact point, but a point well below the critical velocity may easily be selected for use in determining the constants. This, in fact, was the manner in which Pipet 1 was calibrated, as only one point (for water) above the critical velocity was obtained and the exact point at which the critical velocity was exceeded was not accurately determined. With velocities above this region, only the particles nearest the walls of the capillary are moving in parallel motion, while the main volume is in violent, turbulent action.

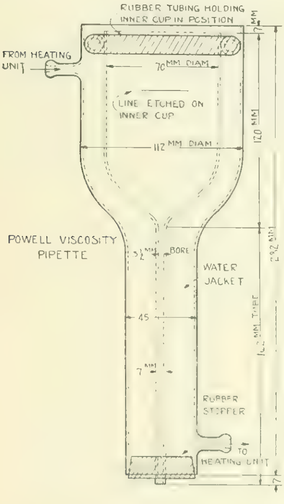

FIG. 4

When the value of the expression $\frac{vd\gamma}{\mu}$, generally known as Reynold's criterion, exceeds a certain figure which is characteristic of each type of viscometer, the change from parallel to turbulent flow has taken place. An attempt has been made to calculate the value of this criterion for the region of critical velocity, but owing to the non-uniformity of the diameter of the glass capillary and other dimensions, an approximation only could be arrived at. For Pipet 1 this region lies near to the value $\frac{vd\gamma}{\mu \text{ (in cp.)}} = 12.00$, which is less than the value 20.00 generally used with the long tube instruments, since the capillary is only 30.5 diameters in length, and is greater than the value 8.00, which is the value calculated for instruments of the short tube type, such as the Engler and Saybolt,[4] where the ratio of length to diameter is about 7.

If only a limited degree of accuracy is desired, the point of critical velocity may be obtained by calculating the A and B constants from a series of low points and a single high point and selecting the pair which will give a correct calculation for a value on the curve immediately below the selected point. For instance, if values for A and B are calculated from a 45 per cent solution of glycerol and a suitable high point and these values suffice to calculate the known viscosity of a 40 per cent solution of glycerol, then it is reasonable to assume that the A and B values are correct. The constants, however, may not be used to calculate viscosities above the critical velocity. About forty pipets of the type described above have been calibrated in this manner, and solutions of unknown viscosities have been evaluated to an accuracy of less than ± 0.1 centipoise. Table II gives a series of viscosity determinations on glue solutions (12.5 per cent, 60° C.) on two pipets calibrated by this method. Portions of the same solution were used with each pipet in order to eliminate any error due to concentration or method of preparation. Pipet 2 was of the same type as Pipet 1, but the running time was considerably less.

TABLE II—VISCOSITY OF GLUE SOLUTIONS DETERMINED BY TWO PIPETS

Glue No.	Pipet 1 Cp.	Pipet 2 Cp.	Difference Cp.
1	15.86	15.97	0.11
3	13.73	13.72	0.01
5	11.83	11.88	0.05
7	10.26	10.11	0.15
9	8.64	8.59	0.05
11	7.40	7.42	0.02
13	6.32	6.24	0.08
15	5.28	5.35	0.07
17	4.46	4.50	0.04
19	3.74	3.73	0.01
21	3.17	3.18	0.01

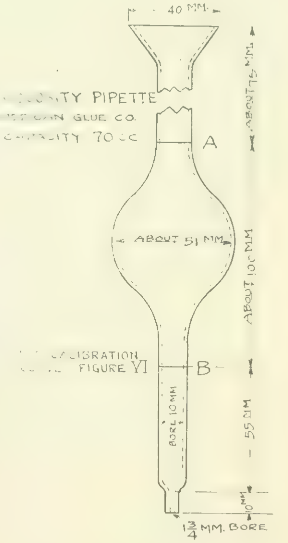

FIG. 5

In order to determine the suitability of a pipet for a given range of viscosity, two other pipets of radically different design were calibrated. The Powell pipet shown in Fig. 4 consists of a cup-shaped glass vessel with attached glass capillary $5^{15}/_{16}$ inches in length, the whole surrounded by a glass water bath. The initial head was adjusted by means of an etched line on the upper part of the cup and the volume delivered was measured by means of an ordinary 200-cc. Engler volumetric flask. The third type of pipet calibrated, which was kindly furnished by George R. Underwood of The American Glue Company, is shown in Fig. 5 and is similar to one shown in Fig. 1 except that the capillary is only 10 mm. long and about 1.75 mm. in diameter. Moreover, the volume delivered was only 70 cc. instead of 100 cc. The A and B constants for each of these instruments were determined and the viscosity of portions of the same gelatin solution determined on each, with the results indicated in Table III.

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[6] Collected Researches, The National Physical Laboratory, **11** (1914)

TABLE III VISCOSITY OF SAME GELATIN SOLUTION BY FOUR PIPETS

VISCOMETER	Seconds	Calculated Absolute Viscosity Cp.
Pipet 1	77.4	13.55
Pipet 2	71.4	13.56
Powell Cup Pipet	74.8	13.61
American Glue Company Pipet, 70 Cc.	59.4	13.94

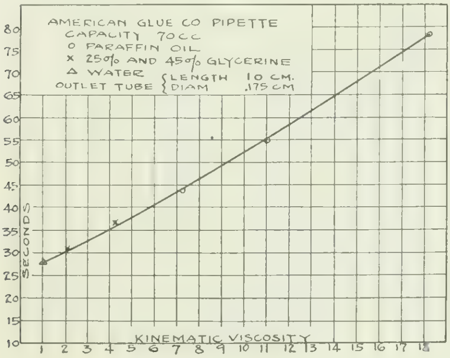

FIG. 6

FACTORS CONTROLLING THE SELECTION OF A PIPET—The calibration curves of the various types of pipets, together with those of the Saybolt and Engler, are sufficient to indicate the importance of the suitability of these types for any particular viscosity determination. The curves for the Engler, Saybolt, and the American Glue Company's pipet are all seen to be quite flat—that is, over the same range of kinematic viscosity the number of seconds "spread" is comparatively low. This is due to the fact that these viscometers are all of the short tube type. On the other hand, the calibration curve for Pipet 1 (Fig. 1), and also the Powell pipet (calibration curve not given, but similar to Pipet 1), shows a wide spread over the same range of viscosity. Both of these are fitted with capillaries of the long tube type. In general, this type is recommended for accurate work, although it must be remembered that the range of viscosities which may be covered is obviously limited. The emergency calibration by the method described above of an ordinary 50 or 100-cc. volumetric pipet may readily be made and accurate viscosities recorded. For a discussion of the factors controlling the selection of the dimension of capillaries reference may be made to the work of Bingham.[7]

THE MACMICHAEL VISCOMETER

The MacMichael torsional viscometer lends itself to determinations of absolute viscosities, but here again we are confronted with a need of practical standardization in order to obtain check results. This investigation has considered a typical calibration of the MacMichael viscometer as it pertains to practical usage in the commercial laboratory. This instrument has been employed with success upon various true liquids and also upon plastic material such as slip clays, starch and rubber solutions, and, recently by Bogue,[8] on glue solutions. It has been described in detail by MacMichael,[9] Herschel,[10] Hayes and Lewis,[11] and the reader is referred to these publications for a complete discussion and calibration of the MacMichael viscometer.

The liquids used in the calibration of this instrument were the same as used for the capillary type. The revolving cup was adjusted to a speed of 56.4 r. p. m. and the larger disk bob and wire No. 32 were used in all determinations. The temperature of 100 cc. of the liquid to be measured was adjusted in the cup after first bringing it near to that temperature at which a reading was to be taken. The conversion curve in Fig. 7 shows that the degrees MacMichael deflection is a straight-line function of the absolute viscosity for all values above approximately 2 centipoises. Readings below this point, as pointed out by Herschel, are affected by turbulence and centrifugal forces, which make the curve tend to curve slightly at the lower end. This is shown more apparent in Fig. 8, where the factor cp./° M.[12] is plotted against centipoises.

TABLE IV—CALIBRATION OF MACMICHAEL VISCOMETER
(Wire No. 32, 56.4 r. p. m.)

Temperature	° M.	Cp.	Conversion Factor
	60 Per cent Sucrose Solution		
60	134	9.83	0.0733
55	148	11.67	0.0789
50	179	14.01	0.0783
45	209	17.18	0.0822
40	248	21.28	0.0858
	40 Per cent Sucrose Solution		
60	41.0	1.98	0.0483
55	43.5	2.22	0.0510
50	46.5	2.50	0.0538
45	49.5	2.85	0.0576
40	53.0	3.25	0.0613
35	59.0	3.76	0.0637
30	64.5	4.38	0.0680
25	75.0	5.19	0.0692
20	88.0	6.20	0.0705
15	103.5	7.47	0.0722
	Distilled Water		
60	18.0	0.47	0.0261
45	20.5	0.60	0.0292
30	23.5	0.80	0.0341
	Medicinal Paraffin Oil		
60	83	5.87	0.0707
45	118	8.96	0.0759
30	185	15.15	0.0819

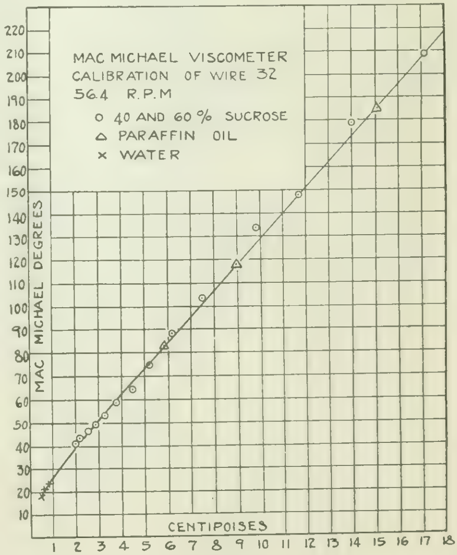

FIG. 7

In order to obtain comparative data on the MacMichael instrument and the capillary type pipet, portions of the same solutions (in duplicate) of three glues were run on two pipets and in the MacMichael viscometer. The calibration curves for each were then used to calculate the absolute viscosity. The data obtained are given in Table V.

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[7] THIS JOURNAL, **6**, 233 (1914); "Fluidity and Plasticity," **1922**, p. 316.

[8] *Chem. Met. Eng.*, **23**, 61, 197 (1920).

[9] THIS JOURNAL, **7**, 961 (1915).

[10] *Ibid.*, **12**, 282 (1920); *J. Optical Soc. Am.*, **7**, 335 (1923).

[11] *J. Am. Soc. Mech. Eng.*, **38**, 626, 1002 (1916).

[12] ° M. = degrees MacMichael.

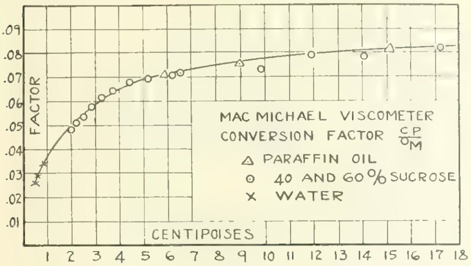

Fig. 8

Table V—Comparative Viscosities by MacMichael Viscometer and Pipets 1 and 2

Glue No.	MacMichael ° M.	MacMichael Cp.	Pipet 1 Sec.	Pipet 1 Cp.	Pipet 2 Sec.	Pipet 2 Cp.
1	148	11.7	55.8	10.15	61.2	10.38
	146	11.5	56.2	10.19	61.2	10.38
		Av. 11.6		Av. 10.17		Av. 10.38
2	107	8.0	44.0	7.52	45.5	7.39
	105	7.8	43.2	7.34	45.8	7.24
		Av. 7.9		Av. 7.43		Av. 7.32
3	162	12.9	64.2	11.95	70.0	12.11
	163	13.1	65.0	12.11	70.4	12.19
		Av. 13.0		Av. 12.03		Av. 12.15

It will be noted in Table V that, while the two pipets check one another very closely, they do not give the same absolute viscosity as the MacMichael instrument. Attention is called to this discrepancy because it brings up a question which is of special interest. Is the viscosity of a colloidal solution dependent on the type of instrument used? Although it may be true that plastic substances like glues at lower temperatures have no constant viscosities, dilute glue solutions such as those used in this work and at a temperature of 60° C. are decidedly fluid substances, and when their previous histories (as in the foregoing cases) are carefully controlled, their apparent viscosities in absolute units appear to vary with the type of instrument used. The discrepancy increases with the grade—that is, with the viscosity. Whether it is due to a breaking down of the colloidal aggregate in passing through the small capillary of a pipet, causing a lower viscosity, or to the fact that a difference in the rate of shear affects the apparent viscosity of colloidal solutions or to a combination of the two, is not definitely known. With the MacMichael instrument the velocity of the solution at any point does not equal the velocity in the capillary, and therefore there is little tendency to damage the colloidal structure with this type. Excessive agitation has been shown to contribute largely to the lowering of the viscosity of glue solutions. In fact, when the operation of running them through a capillary is repeated on the same solution, a lower viscosity is usually observed. On the other hand, the effect of difference in the rate of flow has been observed only on glue solutions of 12.5 per cent concentration at 60° C., where an increase of about 27 per cent in velocity did not appreciably affect the viscosity recorded. However, the absolute viscosities recorded on the pipets for true solutions such as sucrose and glycerol check very closely with those recorded on the MacMichael instrument.

Discussion of Calibrating Solutions

For the calibration of commercial viscometers in absolute units, several liquids and solutions are available whose viscosities are accurately known. Glycerol and sugar solutions have been studied and viscosities which agree very closely have been reported in publications of the Bureau of Standards.[13] With the equipment available in the present commercial laboratory, sucrose solutions containing 20, 40, and 60 per cent sucrose are probably useful only between 10° and 60° C., which gives a viscosity range between 0.81 and 109.8 centipoises. These solutions are readily prepared and standardized either by the density method or by means of the polariscope. The higher concentrations, however, vary in viscosity quite rapidly with a change in temperature, and therefore should be used with due consideration of the limits of error involved. This is the case with glycerol solutions, and to a greater extent. Here the viscosity changes very rapidly above a 55 per cent concentration.

The absolute viscosities of alcohol solutions are also available, and these are especially suitable for calibration purposes on low viscosities. Although alcohol solutions above ordinary temperatures are quite volatile, this fact is offset by the fact that their viscosities change only very slowly with a change in concentration. For the pipet calibrations mentioned above, as has been indicated, a 25 per cent solution of glycerol was used to fix the position of the calibration curve at its lower end, and a highly purified medicinal paraffin oil, the viscosity of which was determined by the Bureau of Standards by request, to fix the upper end of the curve. It will be noted from Table II that the only determination made above this point—namely, that of castor oil at 40° C.—checks remarkably well with the value determined by Kahlbaum and Räber.[14] In general, nonvolatile oils are recommended for calibrating purposes at comparatively high viscosities. The absolute viscosities, when unknown, may be determined by sending about 200 cc. to the Bureau of Stand-

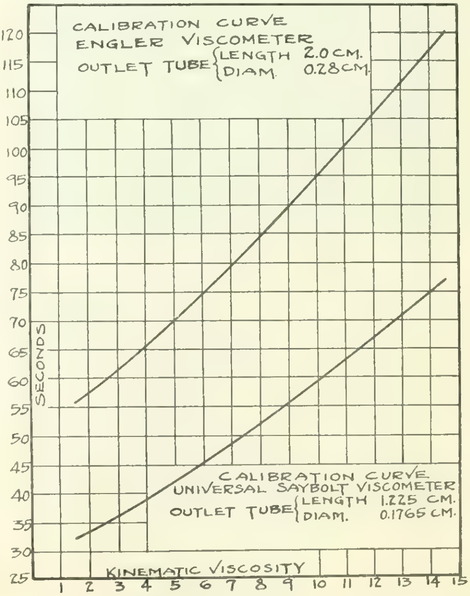

Fig. 9

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[13] *Bur. Standards, Sci. Paper* **298** (1917).

[14] For discussion of viscosities of various castor oils, see *Bur. Standards, Sci. Paper* **112**, 24 (1919).

ards or by an accurate determination on a long tube, calibrated viscometer.

ACKNOWLEDGMENT

The writer wishes to express his indebtedness to J. R. Powell, chief chemist of the Armour Glue Works Laboratory, under whose supervision this investigation was carried out, for his many helpful suggestions and coöperation; to Robert H. Bogue, of Lafayette College, for his aid in the calibration of the MacMichael instrument, and to W. H. Herschel, of the Bureau of Standards, for valuable suggestions and kind review of the paper.

The Control of Motion and Aeration in Corrosion Tests[1]

By J. F. Thompson and R. J. McKay

THE INTERNATIONAL NICKEL CO., NEW YORK, N. Y.

Exact results can be obtained in corrosion tests by liquid immersion when quantitative control of the aeration of the corroding liquid and the motion of the corroding liquid relative to the corroded solid is maintained. Tests made to predict the practical service of factory equipment will be in error unless these important factors are duplicated, or accurately corrected for. Control is more difficult in quiet than in moving tests.[2]

The mechanism by which variation in aeration and rate of motion affects the corrosion rate is discussed. A test method of control sufficiently accurate to reproduce results within about 5 per cent is given. Also, results obtained in connection with a series of 2000 tests on acid-resisting metals in 2 to 10 per cent sulfuric acid, duplicating some conditions found in pickling steel sheets, are presented. The results illustrate an increase in rate of 500 per cent from air-free to air-saturated solution and of 600 per cent from comparative quiet to motion at 0.5 foot per second, but the agreement has been well within 5 per cent with quantitative control of these variables. The results are in accord with experience in pickling practice.

ACID corrosion tests of several "acid-resisting" metals were undertaken at the Mellon Institute of Industrial Research during 1920 to determine the causes of irregularities in the length of service obtained from Monel metal apparatus used for pickling steel sheets. As the tests progressed the control of certain factors was found necessary to obtain accurate results, but in spite of the importance of these factors a search of the literature revealed little or no accurate information regarding them.

A large part of the literature on related subjects discusses tests made by suspending a sample in a solution, making no provision for movement of the solution nor for the prevention of motion. It seemed from the outset that the duplication of results could not be obtained by this method, as it could not compensate for the change in concentration of the corroding agent, which must of necessity take place at the solid-liquid contact. Therefore, an apparatus was planned which would give a positive regulation and control of the relative motion of the sample and the solution, without any very definite idea of just how this movement would affect the mechanism and the rate of corrosion. One of the most generally used machines in pickling sheets produces a motion in the solution of a character suitable for laboratory control, and by copying the motion of this machine it was possible to regulate the movement and at the same time to subject the samples to the same conditions in this respect that obtain in actual service. A laboratory apparatus duplicating this motion was therefore devised.

EFFECT OF MOTION ON RESULTS

After the apparatus was installed, tests were run to determine the difference in the effect of motion or quiet, both from the standpoint of absolute corrosion rate and of reproducibility of results. The quiet and the moving[2] tests were made in all respects under the same conditions, except that in the quiet tests the drive motor of the moving mechanism was shut off.

The results obtained in these tests (Table I) showed such a surprising increase in the rate of corrosion and in the accuracy of results at even low velocities over the rate and accuracy obtained in quiet tests, that the plan of making quiet tests was discarded as useless. They could not furnish a prediction of practical results, nor were they accurate enough for any conclusions.

No increase in the rate was apparent between 0.25 and 0.5 foot per second. The percentage experimental error here is less than was usually obtained, but the usual effect of a much larger error in quiet than in moving tests is found. Of all tests made the average variation was 4.5 per cent for moving tests and 20 per cent for quiet tests.

TABLE I

Air saturation about 15 per cent. Temperature 60° C.
6 per cent sulfuric acid

Motion Rate Ft./Sec.	Corrosion Rate—Mg. Sq. Dm./Day Sample 2649	Sample 2661	Sample 2664	Average	Average Variation[a] Per cent
0.0	26	23	22	24	7
0.125	141	138	139	139	0.7
0.50	140	130	135	135	2.3

[a] Calculated by averaging the percentage variations of single tests from their average. This was found to be a useful measure of accuracy.

As the tests had for their purpose the study of corrosion of metals in the pickling of steel, they were made under conditions as nearly as possible duplicating those of actual pickling practice. The temperatures used ranged from 60° to 90° C., and the concentrations of acid from 2 to 10 per cent of sulfuric acid by weight.

APPARATUS FOR MOTION CONTROL

The movement of the samples relative to the solution was accomplished by the apparatus shown in Fig. 1. Virtual, harmonic, vertical motion was transmitted to a horizontal bar from an electric motor through a belt drive with cone pulleys, worm reducing gear, chain and cone sprockets, and adjustable crank. The motor was 0.5 horse power, 1700 revolutions per minute. The length of vertical stroke of the bar was adjustable in the yoke from a minimum of 0.5 inch to a maximum of 4 inches. The rate of stroke could be adjusted from 3 to 100 revolutions per minute. These adjust-

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[1] Received July 7, 1923.

[2] The terms "quiet" and "moving" are used in preference to "static" and "dynamic," favored by other writers, because the latter properly are used in reference to forces rather than to materials.

ments enabled a variation in the rate of movement of the sample through the solution from 3 to 800 inches per second.

Glass rods, bent in such a shape as to carry the sample with contact at only two places, passed through holes in the bar and were fastened rigidly by thumbscrews. Holes were provided for five rods, and, in cases where no inaccuracies could result from testing more than one sample in the same solution, a frame was used to carry a number of rods. This device furnished a regular and measurable movement, easily adjusted. The samples came into contact with the rod at only two lines, each 0.25 inch in length, and the sample needed no suspension holes or other special shape. The rate of movement was controllable independently of all other factors.

Battery jars with a capacity of about 4 liters were placed in a large water bath on a table under the moving bar, at such a height that the glass rods could be easily set to carry the samples completely immersed, still allowing freedom of movement and easy removal. The table carrying the samples rested on the floor, independent of the frame which carried the motor and other moving parts, so that there would be no vibration to disturb the contact film.

The fact that the motion was noncontinuous was considered a disadvantage, because there was a complete stop and also a maximum rate 50 per cent higher than the average. However, it was considered more satisfactory than a continuous rotation, because the swirling produced by rotation would make the actual velocity past the surface harder to determine. A continuous-flow apparatus to handle the solutions in question at known speeds, possible of regulation within wide limits, was considered too expensive; but, in view of the results obtained, it seems that such an apparatus would pay for itself in results of general value.

Results without Control of Aeration

After the apparatus was operating, results were obtained for a time which checked each other closely. Then unaccountable variations began to appear. Results varied as much as 20 per cent from one day to another, for no apparent reason. Finally, it was noticed that when the laboratory windows were left open in windy weather and there was an appreciable draft of air through the room, results were invariably high. The only obvious way in which this breeze could affect the tests was in blowing the steam away as it arose from the jars and thus coming in contact to a variable extent with the surface of the solutions. No reference could be found in the literature to differences in corrosion rate with an air contact in acid solutions of such a strength, but a consideration of the chemical reactions involved showed that a considerable effect might be expected. Therefore, the following test was devised to check the point:

Several samples of the same alloy were tested in the same solution, placed at different distances below the surface, while especial precautions were taken to keep the solutions quiet. The results were obtained in two typical tests. The distance from the surface as given is the center of the line in which the samples moved. The alloy used was Monel metal and the temperature and concentrations were the same as in Table I.

Table II

Distance from Surface Inches	Test 1 Mg./Sq. Dm./Day	Test 2 Mg./Sq. Dm./Day
0.75	193	152
2.00	173	140
3.25	157	127

If the air contact with the surface affects the rate of corrosion, it would be expected that the samples near the surface would corrode at a more rapid rate than those at the lower levels. That this actually happens is shown with surprising definiteness by the results. The difference between the results of Test 1 and Test 2 is typical of the variations that were being obtained at this stage of the research, but the effect of the greater supply of air near the surface is shown in both.

It was then suggested that if the air had such an important effect a convincing qualitative proof would be to direct a small stream of air against a plane surface of metal and thus possibly produce an indentation at the point of contact. This experiment was tried by connecting the laboratory air line to a water-bottle delivery tube, so arranged under a 6 per cent acid solution that the stream of air was forced at right angles against the sample. The result was that 0.25-inch plate samples of several acid-resisting metals were completely perforated by the air jet before there was any appreciable thinning in the immediate neighborhood of the holes. Photographs of some representative samples are given in Figs. 2 and 3. These results were interesting in that they offered new enlightenment as to the mechanism of the corrosion and they furnished an explanation of certain of the practical phenomena. However, they demonstrated the necessity of control of the air content of the solution, which introduced new experimental difficulties.

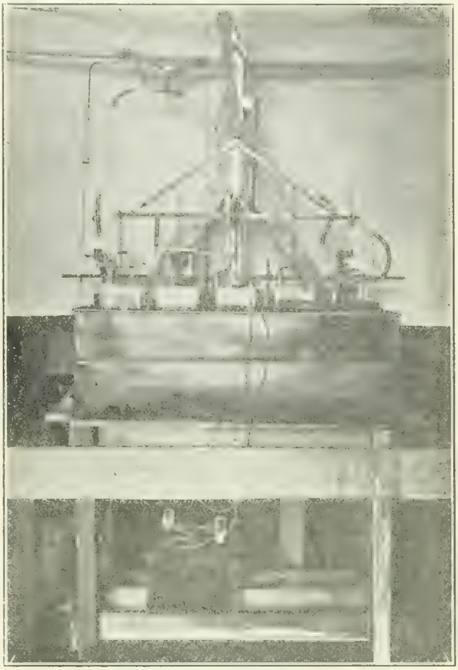

Fig. 1—Front View of the Apparatus

Necessity of Aeration Control

The resistance of so-called "acid-resisting" metals to acid corrosion is due largely to the fact that they do not replace hydrogen in acids. Taking copper, for example, the reaction

$$Cu + H_2SO_4 \longrightarrow CuSO_4 + H_2 \qquad (1)$$

will not proceed in the direction indicated. Consideration of the heats of reaction indicates that the reaction

$$2Cu + O_2 + 2H_2SO_4 \longrightarrow 2CuSO_4 + 2H_2O \qquad (2)$$

will have a greater tendency to take place—in fact, it is exothermic, whereas Equation 1 is endothermic. The evident products of corrosion of copper by sulfuric acid are copper sulfate and water, and it is therefore probable that the reaction proceeds according to Equation 2. Therefore, it would be expected that the rate of reaction would depend on the concentration of Cu, O_2, and H_2SO_4. In other words, dissolved oxygen should be as active in producing corrosion as a strong acid. Copper is here used as an example, but the reasoning will apply to any metal which will not directly replace hydrogen in acids.

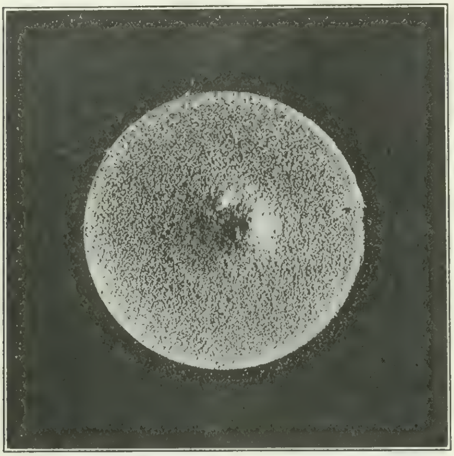

FIG. 2—MONEL METAL PERFORATED BY AIR JET

For metals which will replace hydrogen, the following reactions take place:

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2 \qquad (3)$$
$$2Fe + O_2 + 2H_2SO_4 \longrightarrow 2FeSO_4 + 2H_2O \qquad (4)$$

As above, it would be expected that the reaction velocity would be increased by the presence of oxygen, but in this case both reactions are exothermic and the metal is corroded with considerable speed in both cases. The results given below are in agreement with this reasoning, as shown by the smaller effect of aeration in accelerating the corrosion of iron than of metals of low solution pressure. (Table V)

According to Seidell,[3] the solubility of oxygen from air in water at 25° C. is 0.0075 gram per liter, or about 0.00094 normal. In the present tests the concentrations of acid were from 2 to 10 per cent, or 0.5 to 2.0 normal. The concentration of acid is thus from 500 to 2000 times as great as that of oxygen. At 80° C. this ratio would probably be increased to a maximum of 10,000.

Thus, at the normal corrosion rate for copper in 2 to 10 per cent sulfuric acid, 1000 mg. per sq. dm. per day, a sample of area of 0.5 sq. dm. (an ordinary sheet sample 2 inches square) would exhaust the air from a 200-cc. corroding solution, according to Equation 1, in about 6 minutes, if the corrosion proceeded at the maximum rate. The concentration would be decreased 16 per cent in 1 minute and the rate of corrosion diminished accordingly. This is accompanied by no appreciable change in the concentration of the acid.

Therefore, it would be expected that in such a corrosion the rate would depend very much more on the concentration of air in solution than on the concentration of acid. This has been found to be true in the experiments of the authors.

The oxygen necessary for these reactions may, of course, be furnished by an oxidizing agent, if one is present, or by catalysts. These catalysts may be compounds, such as iron sulfates, which are oxidized readily by oxygen and reduced by metal, or finely divided or colloidal material carrying absorbed oxygen, or, in special cases, a combination of the two, as with the hydrates of iron.[4]

INTERDEPENDENCE OF MOTION AND AERATION

Since the reaction presumably only takes place at the surface of the metal, there is another condition to consider. Instead of the rate of reaction being determined by the concentration in the body of the solution, it is determined by the concentration in actual contact with the surface. As has been seen, the material whose contact must be considered is not the acid but dissolved oxygen. Therefore, a change in the supply of oxygen to this surface determines a change in the rate of motion of the solution and the rate of supply of oxygen to it. Thus, the rate of motion of the solution is of importance in supplying oxygen to the sample, and, within certain limits, the concentration in the contact film will vary with the motion and the rate of corrosion will increase with increase in motion.

Unless there is some continuous motion of the solution, the corrosion products will be unevenly distributed, owing to slight movements of the corroding liquid, and this will produce differences in the concentration of the corroding medium. The differences in concentration will set up quasi-concentration cells[5] which accelerate corrosion at one point and inhibit it in others. Therefore, the corrosion is uneven and such tests do not give duplicate results. A controlled moderate agitation of unvarying speed will largely prevent these effects and enable the reproduction of results. The agitated test is the more practical, because in most service cases of corrosion of acid-resisting metals the corroding medium is in movement.

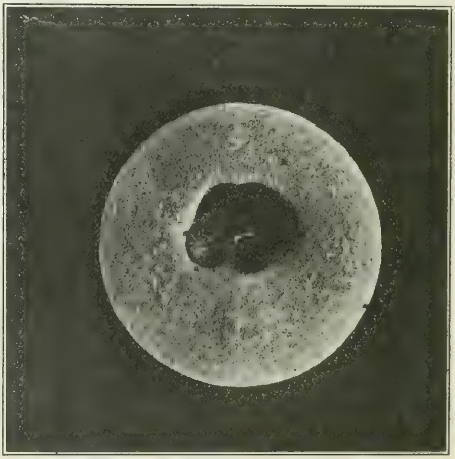

FIG. 3—ALUMINIUM BRONZE PERFORATED BY AIR JET

APPARATUS FOR AERATION CONTROL

In order to produce a known concentration of dissolved oxygen in the corroding solutions, the apparatus shown in

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[3] "Solubilities of Organic and Inorganic Materials," **1917**.

[4] Friend, *Trans. Am. Electrochem. Soc.*, **40**, 1 (1922).

[5] McKay, *Ibid.*, **41**, 201 (1922).

Fig. 4 was developed. An alundum crucible of medium fineness was fitted carefully with a rubber stopper. The stopper was cut thin to insure a perfect fit without breaking the crucible, and over it was placed a wooden disk held by strong, narrow rubber bands passing vertically around the crucible. The disk and stopper were bored to receive a glass tube connected with the pressure gas supply. This arrangement enabled the holding of sufficient air pressure within the crucible to produce a rapid emission of fine bubbles.

In use the stopper was so fitted on a bent glass tube as to lie in the bottom of the battery jar under an inverted glass funnel held on a glass standard. The funnel collected all the bubbles from the crucible and delivered them near the surface of the solution, thus preventing actual contact between the bubbles and the samples. The solution flowed up through the funnel with the bubbles, giving sufficient circulation to assure saturation with gas, but without affecting appreciably the average rate of movement relative to the sample.

It was necessary, in making a test, to use great care that this saturation device was operating at full efficiency. A small crack in the crucible or leak at the stopper allowing an appreciable proportion of air to flow in large bubbles invariably caused low results. The saturated condition was usually indicated by the formation of secondary minute bubbles in the solution from time to time, and unless this happened the saturating apparatus was not considered efficient.

In tests with the solution saturated with air the surface of the liquid was in contact with the laboratory atmosphere. In all others a glass cover was placed over the battery jar and neutral or suitable gas or gas mixtures were used in the saturator. The glass cover was a rectangular plate bored to admit the air tube, siphon, and sample support. Vapor from the warm solution condensed on this cover, sealing any slight openings. Interstices were left sufficient to allow the gas to escape. On the moving sample support a glass tube was fastened with a rubber tube in such a manner that the top end was sealed and the lower end fitted in the hole in the cover so as to seal the opening with a water film and still move freely up and down and allow the necessary play sideways. Thus, by controlling the relative volumes of gas admitted to the saturator, the concentration of oxygen or any active gas could be controlled independent of all other factors.

With apparatus as now developed it was again found possible to duplicate results closely. Some typical results are given in Table III.

TABLE III—MONEL METAL

Rate of motion, 0.25 foot per second

Test	Temperature ° C.	Concentration H_2SO_4 Per cent		Corrosion Rate Mg./Sq. Dm./Day	Average Variation Per cent
Methane used in saturator					
1	82	6		43	
2	100	3		71	
Nitrogen used in saturator					
1	82	10		135	
2		6		152	
3		6		135	
4		2		127	5.3
			Av.	137	
Air used in saturator					
1	82	10		726	
2				686	
3				692	
4				701	1.7
			Av.	701	
1	82	4		652	
2				685	
3				675	
4				682	1.6
			Av.	674	
No saturator. Air in contact with surface of the solution					
1	60	6		107	
2				157	
3				164	
4				194	
5				200	24
			Av.	144	

The much better duplication of results where the saturator was used is of note. The tests without the saturator were made during the first part of the investigation before the importance of the factors in oxygen supply discussed above were realized. The comparatively large variation in these tests resulted in the development of the saturator.

TABLE IV—COLD DRAWN COPPER

Rate of motion, 0.25 foot per second

Test	Temperature C	Concentrated H_2SO_4 Per cent	Corrosion Rate Mg./Sq. Dm./Day
Methane used in saturator			
1	82	6	64
2	100	3	78
Air used in saturator			
1	60	6	1070
2	60	2	1110

The results obtained by using a reducing gas in the saturator were always lower than those wherein nitrogen was used. It is believed that this was because the nitrogen (from commercial tanks) contained a trace of oxygen or a slight amount of air was carried to the solution by drip from the glass cover. With the reducing gas this effect would be minimized.

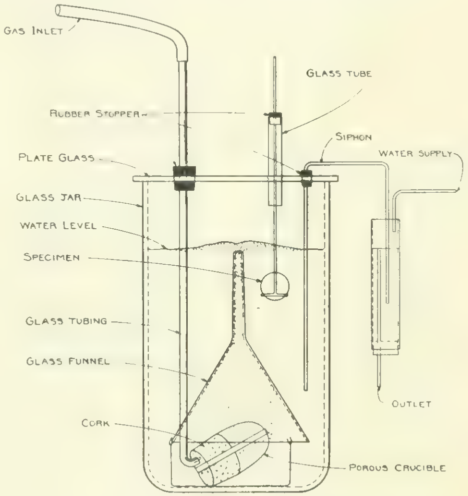

FIG. 4—AERATING APPARATUS

Tests made on about fifteen acid-resisting metals and alloys, with and without the presence of air, showed effects of the same order of magnitude in all cases.

According to the reasoning in this discussion, the effect of oxygen in the corrosion of steel should be less than in the corrosion of Monel metal. This inference was found to be true, and the relative effect on steel was found to be greater in the lower acid concentrations, which observation agrees with the interesting contemporary results of Whitman, Russell, Welling, and Cochrane.[6]

TABLE V—RATE OF SOLUTION OF COLD ROLLED STEEL

Sample	Area Sq. Dm.	Weight G.	Loss	Ratio Loss Mg./Sq. Dm./Hr.	Saturated with	Acceleration by Air Per cent
Test 1: 82° C., 6 per cent H_2SO_4, 5 minutes						
A	0.148	21.7491	0.6851	56	Air	0
B	0.143	18.1341	0.7492	63	Nitrogen	
Test 2: 82° C., 0.05 per cent H_2SO_4, 15 minutes						
A	0.13	20.0935	0.0395	1.21	Air	22
B	0.12	17.0331	0.0296	0.99	Nitrogen	
Test 3: 82° C., 0.05 per cent H_2SO_4, 5 minutes						
A	0.13	19.9352	0.0300	0.92	Nitrogen	
B	0.12	17.1051	0.0341	1.14	Air	24

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[6] THIS JOURNAL, **15**, 672 (1923).

The many other factors which affect the rate of corrosion of metals will not be discussed, but the inadequacy of drawing conclusions from experiments in which agitation and aeration are incompletely controlled is to be emphasized.

The following notes mention briefly some of the other conditions existing throughout the tests. The duration of tests was usually 20 hours. In the absence of serious pitting, the loss in weight per unit surface per unit time was used as the measure of the corrosion rate.

Tests were repeated until the certainty of securing duplicate results was assured. The samples were of a standard size, a disk 1 inch in diameter and 0.25 inch thick. All surfaces were ground with zero emery before testing. Solutions were analyzed before and after all tests. A constant-level siphon furnished water to replace the rapid evaporation. The volume of solution was 3 liters. The sample was set on edge on two glass rods, making contact at only two places. Temperature was maintained by an electrically heated, thermostat-controlled bath covered with paraffin.

This investigation was begun for the purpose of studying certain practical problems and led to their solution before the effect of variation in rate of motion and of concentration of dissolved oxygen were fully determined. The pressure of other practical work has made it impossible to pursue the study with rapidity. It would be desirable to ascertain the effect of rate of motion over a greater range of speeds and the influence of air saturation; also to study other concentrations of dissolved oxygen. The data presented herein are sufficient to show that progress in corrosion study must be accomplished by thorough knowledge of these factors.

ACKNOWLEDGMENT

The authors take pleasure in acknowledging the valuable advice and assistance received from E. Ward Tillotson, assistant director of Mellon Institute of Industrial Research, where the research was conducted by the junior author.

An Application of the Vacuum Tube to Chemistry[1]

By D. F. Calhane and R. E. Cushing

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The following article details a new method of accurately titrating dilute solutions of salt with silver nitrate. The concentrations investigated varied from N/100 to N/2500.

The voltage changes produced in a concentration cell during titration of a solution in one limb of it are impressed on the grid element of the tube.

The changes in potential of the grid vary the value of the plate current through the galvanometer, altering the magnitude of the scale reading of the galvanometer. The end of the titration is shown by no further change in the galvanometer deflection, when more titration reagent is added to the solution in one limb of the concentration cell.

During some work involving the use of the well-known Mohr reaction, it became necessary to employ this in the titration of very dilute solutions of salt, obtained as a discharge from the test of a 3000-horse power turbine. As may be remembered, this method employs a solution of nitrate of silver that is added to precipitate the chlorine in a neutral solution as silver chloride. The end of the titration is indicated by a red color, due to the formation of silver chromate in presence of potassium chromate as an indicator.

Under favorable conditions this is a very accurate titration. In the presence of any colored impurity in the water, or considerable precipitated silver chloride, the observance of the red color, or end point, is a matter of considerable difficulty. It then becomes necessary in some cases to remove the color of the water by chemical means.

It occurred to the writers that they might employ the three-electrode tube, so widely used in radio work, as a means of indicating the end point, without the necessity of relying on any color change.

It was found on consulting the literature that W. A. Noyes, Jr.,[2] had described a use of the three-electrode tube for the measurement of potential in an electrolytic cell for the deposition of iron. This avoided the shunting of an appreciable amount of current around the cell as would be the case when an ordinary voltmeter is used.

A brief description of the manner in which a three-electrode tube functions will make clearer the method of procedure in this work.

FUNCTION OF THREE-ELECTRODE TUBE

In the three-electrode tube a filament of fine wire, plain, or oxide-coated, is heated to a high temperature by a battery current. The high vacuum inside the tube allows negatively charged particles or electrons to be shot off from the hot filament. These electrons are drawn over to a positively charged plate, the second element of the tube. The positive charge on the plate is produced by connecting it with the positive terminal of a second or plate battery. The negative terminal of this plate battery is connected with the negative side of the filament circuit. This provides a path for a current from the plate to the filament. If a galvanometer or milliammeter is connected into this circuit, a current will be indicated from the plate to the filament; the value of this current, within certain ranges, will be dependent on the magnitude of the filament current that conditions the temperature of the filament and the consequent flow of electrons.

If a third element, or grid, is placed between the filament and the plate, a means of controlling the magnitude of the plate current in two directions is available. If the grid is given a positive charge, it will attract negative electrons from the filament. A current will also be established in the grid circuit. If the grid is made negative, a reverse effect will be obtained and the plate current will be decreased for a given change in the potential of the grid. With a negative charge the grid, located between plate and filament, repels the negative electrons from the filament back to the filament, and thus reduces the value of the plate current in proportion to any change that may occur in the value of the negative potential of the grid. These changes in value of the plate current will be indicated by a galvanometer in the plate circuit. A means is thus obtained of noting any very small changes of potential that may occur in any system inserted in the grid circuit.

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[1] Received January 27, 1923.

[2] "Some Aspects of Electrolytic Iron," *Trans. Am. Electrochem. Soc.*, **40**, preprint (1921).

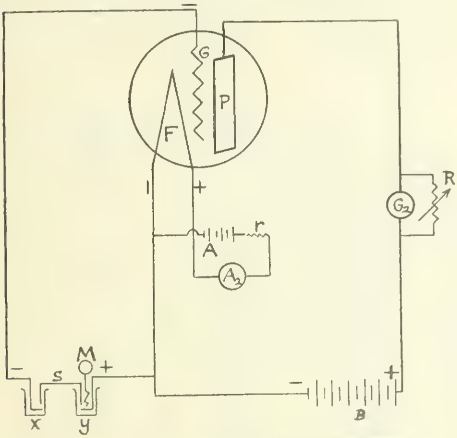

FIG. 1—APPARATUS FOR TITRATION OF SALT SOLUTIONS

F = Tube filament
G = Grid
P = Plate of tube
G_2 = Galvanometer
R = Variable resistance box
B = Plate battery
A = Filament battery
r = Filament rheostat
A_2 = Filament ammeter
x and y = Two limbs of concentration cell
S = Agar filled siphon
M = Motor stirrer

(The solution to be titrated is in limb y)

About a year ago a conductivity cell was tried in the grid circuit. The idea was to titrate out the salt in the usual way, and rely on a change in resistance of the cell to alter the grid potential. This scheme proved fundamentally inoperative since no current flows in the grid circuit when the grid is negatively charged; therefore, a change in resistance of the titration cell would cause no perceptible voltage change on the grid.

The idea that a concentration cell connected in the grid circuit would function in the way desired was found to be correct. This forms the basis of this new method of titration.

PRINCIPLE OF CONCENTRATION CELL

With this device there are two electrodes dipping in solutions of different strength, each electrode and solution in a separate container. When these two single cells are connected by a conducting siphon, a battery is formed, which affords a feeble current from the more dilute solution to the more concentrated, thence through the external circuit back to the electrode in the more dilute solution. The current will flow as long as there is a difference in concentration between the two solutions. The energy that affords voltage to propel a current is seated in a change of osmotic pressure that continually goes on during the equalization of the concentrations. When the concentrations are completely equalized in the two parts of the cell, no further voltage changes, and consequently current flow, will occur.

APPLICATION TO SALT TITRATION

The writers were interested in making use of the change in potential of the electrode dipping in the salt solution of unknown strength. This concentration was to be continually altered by titrating out the chlorine of the salt with silver nitrate in the usual way. A concentration cell was made up of two small beakers, connected by a siphon of solidified agar, which contained $N/10$ potassium nitrate to give conductivity. In the known limb of the cell was a silver wire dipping in $N/10$ potassium chromate saturated with silver chromate. There might also be used here a dilute solution of sodium nitrate saturated with silver chloride plus one or two drops $N/100$ silver nitrate. In the other cell or beaker was a silver wire dipping into the unknown salt solution whose strength was to be determined by titration with silver nitrate.

By connecting this cell in the grid circuit of the three-element tube so that a change in the negative potential of the grid would be produced as the titration proceeded, a means of determining the end point electrically would be provided by the indications of the galvanometer in the plate circuit.

To explain this more completely, as chlorine is precipitated by titration in one limb of the concentration cell, the electrode potential in that arm will increase, owing to removal of chlorine ions. This will cause an increase of the negative potential on the grid, which produces a reduction of the plate current in the tube, shown by a diminishing change in the galvanometer reading.

Very close to the end point, the chlorine will be removed relatively at the fastest rate, causing a rapid and marked potential change of the grid, denoted by wide changes in the galvanometer reading. Practice confirmed this theory. When the end point was reached there was no further change in the concentration cell potential of any significant value, and any pronounced galvanometer variations ceased.

A diagram of the apparatus is given in Fig. 1. An oxide-coated filament tube was mostly used, although an amplifying tube served just as well, by making more careful adjustment of plate potential. With the oxide filament, a 4-volt battery could be used, with a controlling rheostat in the filament circuit. A 22.5-volt plate battery of the type used in radio operation was connected in the plate circuit, as well as a D'Arsonval galvanometer.

The concentration cell was inserted in the grid circuit of the tube, the negative pole being connected with the grid. The silver nitrate solution was run from a buret into the arm of the concentration cell containing the unknown salt solution. This solution was stirred vigorously by a motor-driven stirrer. A resistance box was placed across the galvanometer, to function as a variable shunt, so that the initial value of the plate current could be adjusted to a magnitude below that causing an off-scale deflection of the galvanometer.

The sensitiveness of this method depends on the relative effect that a given change in grid voltage has on the value of the plate current, since the greater this change in plate current effected by the grid variation in voltage, the larger will be the galvanometer deflection.

AMPLIFYING FACTOR

These points may be more clearly expressed by considering what is known as the amplifying factor of a three-electrode tube, and the curve that expresses the relationship between plate current and grid voltage variations, for a constant plate voltage.

The amplifying factor equals plate volts change for a given plate current change divided by grid volts change for the same plate current change. This may be succinctly expressed by the expression

$$u = \frac{\frac{dI_p}{dE_g}}{\frac{dE_p}{dI_p}}$$

As operated, there is a fixed plate voltage in the tube, with a resulting plate current for a fixed filament current, for any one condition. As the grid voltage changes owing to any external cause the plate current varies by a certain amount referable to the amplification factor. The factor for the tube used was about 5.

In order to have these plate current variations as great as possible for a minimum grid voltage change, the constant grid potential for any fixed condition of the system should lie on the steepest portion of the grid-voltage-plate-current curve of the electron tube. Such a set of curves for the tube used in this work is shown in Fig. 2. The plate voltage was 23.7 volts and the filament current 1.1 amperes. This gives a desirable grid voltage swing or variation from −1 to +1 volt, on the steep portion of the plate-current-grid-voltage curve.

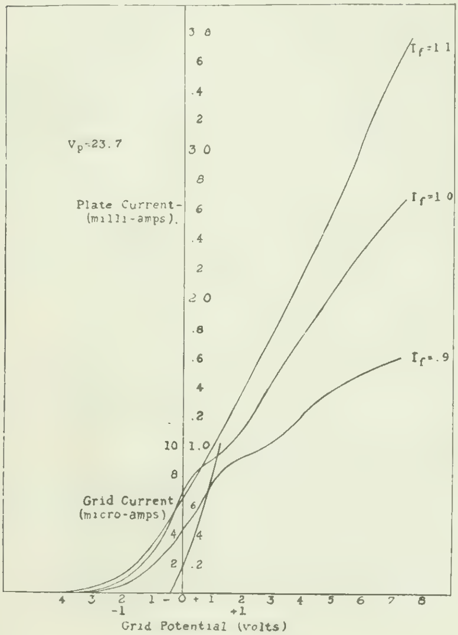

FIG. 2

RESULTS

To show the working of this method, a tabulation of a typical set of results will be most convincing. A salt solution is titrated whose strength in salt is continually diminished. The amount of this solution is listed, and the variation of the galvanometer indicated. Solutions varying in strength from *N*/100 to *N*/2500 are listed. This means a variation of the salt concentration from 5.85 mg. in 10 cc. of 0.01 normality to 0.936 mg. of salt present in 40 cc. of 0.0004 normality. In all titrations the galvanometer makes the most of the swing noted on the addition of last three or four drops of the silver nitrate added to effect the end point. This is in accordance with the theory of the concentration cell.

Ordinary colors in natural waters give no interference with this method. The end point could be more accurately attained on known solutions than with the potassium chromate indicator. This removes the personal equation in the observance of color.

In Expt. 21 the salt solution was colored with methyl blue. In Expt. 23 the end point with potassium chromate was distinguishable only at 5.8 cc.; in Expt. 24, 4.7 cc.; Expt. 37, 4 cc.; and Expt. 39, 3.6 by the same method.

The values in Column 5 are calculated for pure salt in distilled water. Where faucet water was used for volumes of 30 to 40 cc. salt solution titrated, these values should be increased by 0.3 to 0.4 cc. to account for chlorine in natural water. In Expts. 43 to 51 it took 0.3 cc. more silver nitrate, or an average of 2.7 cc., to get red color with silver chromate. Faucet water was used instead of distilled water, as an estimation of total chlorine in salt added plus that in the natural water was desired.

TABLE I—TITRATION VALUES

Expt.	Salt Strength	Solution Volume Cc.	Volume 0.01 *N* Silver Nitrate Observed Cc.	Volume 0.01 *N* Silver Nitrate Calculated Cc.	Galvanometer Swing in Scale Cm.	
1 to 11	*N*/100	10	Av. 10.00	10.0	5.4	
12, 13	*N*/100	20	Av. 20.10	20.0	4.6	
14, 15	*N*/200	10	Av. 5.00	5.0	5.0	
16, 18	*N*/300	10	Av. 3.20	3.33	5.0	
19	*N*/400	10	2.60	2.5	6.0	
20	*N*/400	20	5.10	5.0	5.7	
21	*N*/400	10	2.60	2.5	6.2	
22	*N*/400	20	5.15	5.0	5.0	
23	*N*/400	20	5.10	5.0	5.5	
24	*N*/500	20	4.10	4.0	10.6	
25	*N*/700	20	3.00	2.87	5.2	
27	*N*/700	20	3.05	2.87	3.7	
28	*N*/700	20	3.00	2.87	4.0	
29	*N*/700	20	3.05	2.87	4.5	
30	*N*/700	20	3.10	2.87	4.3	
33	*N*/1000	20	2.15	2.00	4.5	
36	*N*/1000	30	3.20	3.00	3.6	
37	*N*/1000	30	3.10	3.00	3.6	
38	*N*/1000	30	3.10	3.00	3.4	
39	*N*/1500	40	2.80	2.7	3.9	
40	*N*/1500	40	2.80	2.7	3.9	
41	*N*/1500	40	2.90	2.7	3.7	
42	*N*/1500	40	2.80	2.7	3.8	
43 to 51	*N*/2000	40	Av. 2.10	2.0	3.2	(Av. 7 expts.)
52	*N*/2500	40	1.70	1.6	3.0	
53	*N*/2500	40	1.75	1.6	3.0	
54	*N*/2500	40	1.70	1.6	3.0	

With a *N*/2500 salt solution, 1 cc. of *N*/1000 salt solution is equivalent to 25 cc. of *N*/2500 strength. So 40 cc. of *N*/2500 are equivalent to 1.6 cc. of the *N*/100 strength.

The faucet water used to make up the solutions required between 0.3 and 0.4 cc. *N*/100 silver nitrate, and gave a visible turbidity of silver chloride. The agreement is thus sure to be close enough to establish the accuracy of the method.

Even with 40 cc. of tap water, the galvanometer gave a readable deflection of 0.7 cm., which goes to show the extreme sensibility of the method. The galvanometer variation from Expts. 36 to 54—*N*/1000 to *N*/2500 for average of 40 cc.—is only about 1-cm. scale. The decrease in sensibility of the galvanometer is very slow as dilution proceeds.

Work along these lines will be pursued in this laboratory.

Use of Glue in Paper Coating

The Bureau of Standards is conducting some experiments on the use of glue in coating paper. During the past month nine runs have been made on the experimental coating machine, using two makes of bone glue for eight of the runs and a French casein glue for one. The clay used for all runs was Lee Moor, a good grade of English coating clay. The results indicate that the water resistance of glue-bound coating containing chrome alum compares favorably with that of casein-bound paper containing no formaldehyde. It is believed that the degree of waterproofness will prove sufficient for most of the papers used for halftone printing. Difficulties have been experienced in obtaining a uniform coating, because of variation of the fluidity of the coating mixture and mechanical defects in the machine, so that additional work will be necessary before paper suitable for printing test can be produced.

The sum of $1500 has been placed at the disposal of the College of Agriculture of the University of Wisconsin by the Sewerage Commission of the City of Milwaukee for the establishment of a fellowship to study the best methods of using activated sludge as a fertilizer. This material is prepared in large quantities as a by-product in the disposal of Milwaukee sewerage. O. J. Noer has been appointed to the fellowship, which will be under the jurisdiction of the soils department.

Fabric Stresses in Pneumatic Tires[1]

By **H. F. Schippel**

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It has been claimed more than once that tire designing can never become an exact science. No two tires have the same career of service. To estimate with any degree of precision the life history of a tire would be quite impossible. The tire engineer would certainly find it much easier to give anathematical rather than mathematical expression to the effect upon a tire of every obstruction encountered on the road. Experience teaches most of them that too often science and the tire part company forever at the precise instant that the tire falls into the hands of the ultimate consumer.

But to say that tires cannot be built upon sound scientific principles and the various parts balanced according to exact engineering calculation would be to disparage the growth of a tire science that is already in the embryonic stage. The chemist, physicist, and engineer, each has his contribution to make to this science. The chemist has done, and is still doing his part, and is contributing his work to the chemical literature. But of the intricate work of the physicist and the engineer we hear deplorably little. Their work is embodied in the finished tire that leaves the factory. The many indications of astute scientific application in these tires attest the progress that is being made. Whether the result is achieved by the process of experiment or by mathematical calculation is not often clear. But there is no doubt that the latter method would often shorten the toil and expense of the former, by eliminating unnecessary and condensing the necessary experiment, and thereby accelerating the conclusion.

It is with the foregoing thoughts in mind that the writer presents this mathematical analysis of fabric stresses in pneumatic tire carcasses, and while it covers but a small part of the field of tire design, it is hoped that opportunity will occur in the future to offer similar analyses of other complex problems that confront the tire designer.

The definite commensurable stresses to which the fabric of a tire carcass is subjected are the following, which will be called static or dynamic according as they occur when the car is at rest or in motion: Static—(1) stresses due to inflation pressure, (2) stresses due to deflection under load; Dynamic—(3) traction and braking stresses, (4) centrifugal stresses.

There are, in addition, those indeterminate stresses due to road shocks. Their magnitude cannot easily be calculated, and the tire must be more or less safeguarded against them by an adequate factor of safety. But a liberal factor of safety can never successfully conceal an ignorance of the fundamentals of tire design. The reason is simple. The tire may successfully withstand the severe shocks which usually occur only a relatively small number of times, but there is a great danger that it may eventually be destroyed by the insidious action of an oft-repeated minor stress caused through faulty design.

Stresses Due to Inflation Pressure

A tire carcass is essentially a cylindrical vessel containing air under pressure. There are two principal stresses in an inflated hollow cylinder made of thin homogeneous material—the transverse stress, and the longitudinal stress.

Let P = internal air pressure
D_T = internal diameter

Then the transverse stress S_T[2] per inch of axial length

$$= \frac{PD_T}{2} \qquad (1)$$

and the longitudinal stress S_L per inch of transverse periphery

$$= \frac{PD_T}{4} \qquad (2)$$

The transverse is the major stress, and is double the longitudinal stress.

But in the tire these simple stress equations are complicated by five considerations: (1) elliptical transverse section of the inflated tire, (2) inflation stress in the tube, (3) toroidal shape of the tire, (4) fibrous grain of the carcass, and (5) carcass thickness. All these factors vary with each different size of tire, and the true value of fabric stress can be obtained only by calculating the effect of each factor.

1—The cross-sectional shape of an inflated tire is usually elliptical, the major axis having a direction parallel to the axis about which the tire revolves. This ellipticity is a function of the principal diameter of the tire and of the angle at which the fabric threads lie in the carcass. Its effect is to decrease the transverse fabric stress in the same way that a flattening of the ideal hollow cylinder would diminish the transverse stress S_T. The effective diameter D_T of the cylinder for the purpose of transverse stress calculation becomes the minor axis of the elliptical section.

2—The actual pressure per unit area acting upon the inside of the carcass is less than the inflation pressure by the amount of pressure necessary to inflate the tube to fit the inner walls of the carcass.

Let P_T = the pressure necessary to inflate the tube
Then the pressure acting upon the carcass = $P - P_T$ (3)

The value of P_T may be approximated by testing a tube already manufactured, or may be derived mathematically as follows:

Let L_c = internal cross-sectional perimeter of the surface of the inflated tire against which the tube must bear
L_T = cross-sectional perimeter of the outer surface of the noninflated tube
t = tube thickness
m = average elastic modulus of tube stock up to the strain of normal inflation

Then the strain per unit of transverse perimeter of tube

$$= \frac{L_C - L_T}{L_T}$$

and the stress per unit of circumferential length of tube

$$= mt\left(\frac{L_C - L_T}{L_T}\right)$$

and the tube inflation pressure P_T

$$= \frac{2\pi}{L_C}\, mt\left(\frac{L_C - L_T}{L_T}\right)$$

$$= 2\pi\, mt\left(\frac{L_C - L_T}{L_C L_T}\right) \quad \text{(See appendix)} \quad (4)$$

3—The toroidal shape of the tire presents another complexity.

The longitudinal stress S_L remains unchanged (Equation 2),

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[1] Received July 26, 1923.

[2] Burr, "Elasticity and Resistance of Materials of Engineering," **1915**, p. 197.

but the transverse stress S_T becomes

$$\frac{D_T D_R(P-P_T)}{2(D_R + D_T)} \tag{5}$$

for the synclastic part of the tire under the center of the tread, where D_R = the principal diameter of tire to the sectional major axis, or in general

$$S_T = \frac{D_T D_R(P-P_T)}{2(D_R + 2H)} \tag{6}$$

for any point on the carcass distant H from the sectional major axis, positive in the direction of the tread, and negative in the direction of the bead.[3] This effect diminishes the fabric stresses toward the tread region.

4—The fibrous grain of the carcass has a most important bearing upon the fabric stress values. The tire carcass is made of bias-laid fabric, through which the transverse and longitudinal stresses transmit interfering components.

To obtain the component along the fabric threads at any point on the carcass of the transverse stress S_T, consider a unit length AC (Figs. 1 and 2) of the carcass parallel to the longitudinal axis. The force acting perpendicularly on this unit length AC is the transverse stress S_T.

Let F = the integral of the reacting force in the threads crossing AC in each direction, respectively
Θ = the angle between the threads and the line AC
N = number of plies of square-woven fabric, or pairs of plies cord fabric; then

$$S_T = 2FN \sin \Theta \tag{7}$$

$$\text{or} \quad F = \frac{S_T}{2N \sin \Theta}$$

Substituting the value of S_T from Equation 6

$$F = \frac{D_T D_R(P-P_T)}{4N(D_R + 2H) \sin \Theta} \tag{8}$$

But the force F acts over a width of fabric CD, measured perpendicularly to the direction of the threads, so that the force F_1 per unit width of fabric becomes

$$F_1 = F\frac{AC}{CD} = F\frac{AC}{AC \sin \Theta}$$

$$= \frac{F}{\sin \Theta} = \frac{D_T D_R(P-P_T)}{4N(D_R + 2H) \sin^2 \Theta} \tag{9}$$

It is now necessary to consider the distortion of the fabric to conform to the curvature of the carcass. When the fabric suffers an angular distortion, the number of threads per unit distance measured perpendicularly to their direction is increased or decreased according to the angle at which the fabric was originally cut, and the deformation received in building the carcass.

Let B = angle between cutting line and fabric selvage

Considering the distortion of a parallelogram, whose sides are parallel to the two thread directions, respectively,

Let the larger undistorted internal angle = $2B$, and the corresponding distorted angle = 2Θ

Then the ratio of the thread densities,

$$\frac{\text{Distorted density}}{\text{Original density}} = \frac{\sin 2(90-B)}{\sin 2(90-\Theta)} = \frac{\sin 2B}{\sin 2\Theta} \tag{10}$$

and the fabric stress per unit width of original fabric is the inverse of this ratio. Therefore, the stress F_4 per unit original width of fabric

$$F_4 = \frac{(P-P_T)D_T D_R}{4N(D_R + 2H) \sin^2 \Theta} \times \frac{\sin 2\Theta}{\sin 2B} \tag{11}$$

This equation can be simplified for the purpose of calculating the stress in any specific instance by expressing the angle Θ in terms of the angle B and fabric stretch.

Let S = ratio of stretched to unstretched length of the fabric at the extreme ply diameter; then it can be proved that

$$\Theta = \cos^{-1}\left\{ S \cos B \left(\frac{D_R + 2H}{D_R + D_T}\right)\right\} \tag{12}$$

(See appendix)

Equation 11 enables us to calculate the average value per ply of the component of transverse stress S_T acting along the direction of the fabric threads in the zone AC. This component F_1 acts in such a way as to shorten the circumferential length of the tire and shrink it on the rim, thereby producing the characteristic elliptical cross-sectional shape of the tire, and relieving the bead of no inconsiderable amount of stress. It is to be noted that as the zone under consideration approaches the tread region of the tire, H increases and Θ decreases, so that the variations of these two coefficients produce opposite effects, but that due to the variation of fabric angle is by far the greater.

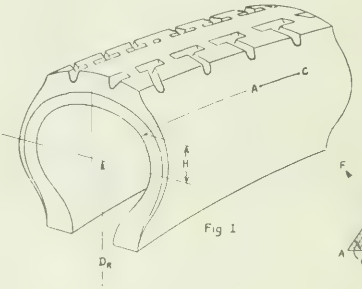

Fig 1

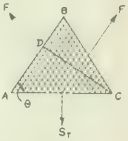

Fig 2

It is interesting to observe the combined effect of the angle B and stretch S, as shown by the curves in Fig. 3A. These curves refer to the maximum fabric stress, which occurs on the inner ply underneath the center of the tread.

At this point $D_T = 2H$, so that $\cos \Theta = S \cos B$.

One is impressed by the apparently large range of choice of fabric stress. Were inflation stress the sole consideration, one would naturally choose as low a value as would be consistent with high manufacturing efficiency. But consideration must also be given to other stresses to which the carcass is subjected, which are also a function of the bias angle and fabric stretch. These stresses will be determined later.

By a process similar to that by which Equation 9 was derived, and elaborating upon the simple Equation 2, it can be shown that the component F_2 of the longitudinal stress S_L acting along the fabric threads is

$$F_2 = \frac{(P-P_T)}{8N} \sqrt{a D_T} \sec^2\Theta \frac{\sin 2\Theta}{\sin 2B} \tag{13}$$

(See appendix)

where a = major axis of cross-sectional ellipse

The longitudinal component opposes the transverse component, and being the smaller force, its sole effect is to reduce the intensity of the contracting force of the tire on the rim. It does *not* reduce the fabric stress.

By equating the longitudinal to the transverse stress and solving for the angle Θ, it will be found that the fabric angle, for which there is no resultant contractive force of the tire on the rim, approximates very closely to the angle 54.7 degrees, which is the "angle of repose" for the ideal right circular cylindrical vessel. For this fabric angle the inflated carcass would have a circular, not an elliptical, cross section. On account of the toroidal shape of the tire, the fabric angle is not uniform, but varies from tread to bead, so that the average fabric angle should equal the "angle of repose."

5—In deriving the foregoing equations of ply stresses in a tire carcass, we have considered the tire as an ideally thin vessel, and the stresses equally divided among all the plies.

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[3] Poynting and Thomson, "Textbook of Physics. Properties of Matter," **1909**, p. 145.

A tire carcass, however, has a considerable thickness as compared with its other dimensions, and this thickness causes an unequal distribution of the inflation stress throughout the carcass.

Let E = cross-sectional ellipse perimeter at median line of noninflated carcass
dE = increase of E due to inflation
T = thickness of one square-woven ply, or of one pair of cord plies

Then, because all the plies are bound together by the rubber skim coats,

the transverse elongation of all plies $= dE$
the unstrained length of first or inner ply $= E-\pi T(N-1)$
that of the second ply $= E-\pi T(N-3)$
that of the third ply $= E-\pi T(N-5)$
that of the Xth ply $= E-\pi T[N-(2X-1)]$

Therefore, the strain per unit transverse length of first ply

$$= \frac{dE}{E-\pi T(N-1)} \qquad (14)$$

that of the second ply

$$= \frac{dE}{E-\pi T(N-3)} \qquad (15)$$

that of the Xth ply

$$= \frac{dE}{E-\pi T\,[N-(2X-1)]} \qquad (16)$$

Let M = average elastic modulus of the fabric up to strain dE

Then the transverse ply stress

$= M.$transverse ply strain

the transverse stress on the first ply

$$= \frac{M.dE}{E-\pi T(N-1)} \qquad (17)$$

$$\text{that on the Xth ply} = \frac{M.dE}{E-\pi T\,[N-(2X-1)]} \qquad (18)$$

To obtain the fabric stress per unit width of fabric, it is only necessary to multiply the right-hand sides of these equations

$$\text{by } \frac{1}{2\sin^2\Theta} \times \frac{\sin 2\Theta,}{\sin 2B} \text{ so that}$$

fabric stress in the first ply

$$= \frac{M.dE}{E-\pi T(N-1)} \times \frac{1}{2\sin^2\Theta} \times \frac{\sin 2\Theta}{\sin 2B} \qquad (19)$$

and that in the Xth ply

$$= \frac{M.dE}{E-\pi T\,[N-(2X-1)]} \times \frac{1}{2\sin^2\Theta} \times \frac{\sin 2\Theta}{\sin 2B} \qquad (20)$$

For the small values of N such as occur in tires, the stress equations for the consecutive plies may be taken as an arithmetic series, having an average value of

$$\frac{M.dE}{E} \times \frac{1}{2\sin^2\Theta} \times \frac{\sin 2\Theta}{\sin 2B} \qquad (21)$$

Equating this to the average fabric stress as derived in Equation 11,

$$\frac{D_T D_R(P-P_T)\sin 2\Theta}{4N(D_R+2H)\sin^2\Theta\sin 2B} = \frac{M.dE}{E} \times \frac{1}{2\sin^2\Theta}$$

and transposing

$$M.dE = \frac{D_T D_R\,E(P-P_T)}{2N(D_R+2H)} \qquad (22)$$

Substituting this value of $M.dE$ in Equation 20, we obtain the general expression for fabric stress F_P in the Xth ply of

$$\frac{D_T D_R\,(P-P_T)}{2N(D_R+2H)} \times \frac{E}{E-\pi T\,[N-(2X-1)]} \times \frac{1}{2\sin^2\Theta} \times \frac{\sin 2\Theta}{\sin 2B} \qquad (23)$$

This is a complete expression for ply stress involving the five tire complexities of elliptical transverse section, tube inflation, toroidal shape, fibrous grain, and carcass thickness.

To check the accuracy of this stress equation, and to illustrate its application to a definite tire, let us calculate the internal bursting pressure of a 33 x 4 straight-side cord tire, and compare with the pressure obtained by actual test. The point of maximum fabric stress occurs at the inner ply, underneath the center of the tread.

P = 60 pounds per square inch = normal inflation pressure
P_T = 4 pounds per square inch = pressure to inflate tube
D_T = 3.92 inches = minor axis of cross-sectional ellipse at median line of normally inflated carcass
D_R = 29.56 inches = principal diameter of tire, to major axis of inflated cross-sectional ellipse
E = 11.7 inches = cross-sectional ellipse perimeter at median line of noninflated carcass
N = 3 = number of pairs of cord plies
H = 1.96 inch = distance from the sectional major axis of the point, on the carcass median line, at which the stress is to be calculated
T = 0.090 inch = thickness of one pair of cord plies
X = 1 = the number of the double ply for which the stress is to be calculated, counting outward from the inner pair of plies
Θ = 33.5 degrees = angle between the cords and a line parallel to the longitudinal tire axis
B = 45 degrees = angle of bias cut

Then the maximum fabric stress $F_P =$

$$\frac{3.92 \times 29.56(60-4)}{2 \times 3(29.56+3.92)} \times \frac{11.7}{11.7-3.1416 \times 0.090(3-1)} \times \frac{2 \times 0.551^2}{1} \times \frac{0.920}{1.00}$$

$= 32.3 \times 1.051 \times 1.649 \times 0.92$
$= 51.5$ pounds per inch width

The fabric strength per inch = 18.0 pounds per cord × 23 cords = 414 pounds

Therefore, bursting pressure $= \frac{414}{51.5} \times 56 = 451$ pounds per square inch

A correction must here be made to allow for the increased fabric stretch from normal inflation to bursting inflation.

Fabric stretch at 60 pounds inflation = 6.3 per cent
Fabric stretch at failure = 18.0 per cent

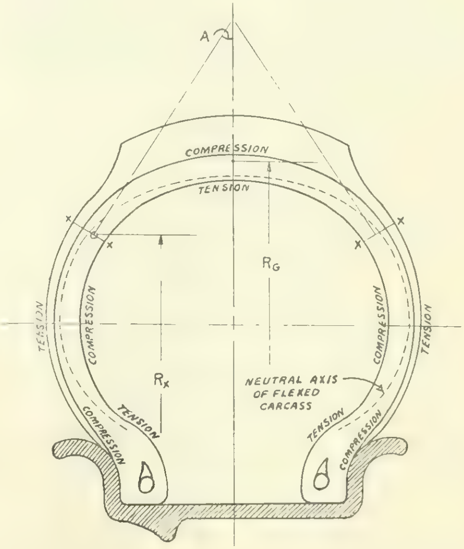

Fig. 3

This increased stretch increases the minor axis D_T, and reduces the bursting pressure.

True bursting pressure $= 451 \times \frac{1.063}{1.180} = 406$ pounds per square inch.

By actual hydraulic test, the bursting pressure was 388 pounds per square inch.

It may readily be calculated that the maximum fabric stress on the second pair of plies is 49.1 pounds per inch width, and on the third pair of plies, 46.7 pounds per inch width.

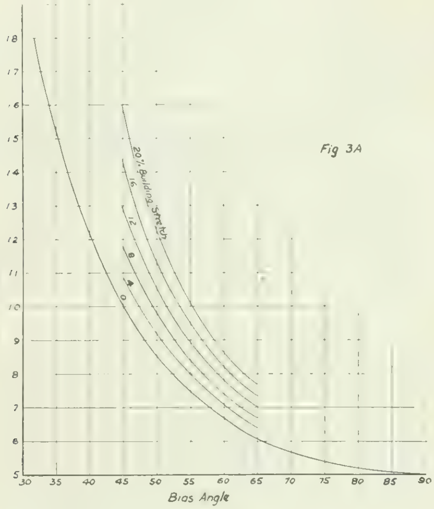

Fig 3A

It will be interesting to calculate the pressure gradient in the tire carcass. The air presses against the inner ply with a force of 60 pounds per square inch, less the tube inflation pressure of 4 pounds per square inch. On the outside of the carcass there is no pressure. The share of the inflation pressure that each pair of plies carries, is

$$K \times \frac{2S_x}{R}$$

where S_x = fabric stress
R = transverse radius of curvature of each pair of plies
K = a constant

Therefore, the inflation pressure $(60-4)$

$$= K\left(\frac{2 \times 51.5}{\frac{3.92}{2} - 0.09} + \frac{2 \times 49.1}{\frac{3.92}{2}} + \frac{2 \times 46.7}{\frac{3.92}{2} + 0.09}\right)$$

$$= K\ (55.1 + 50.1 + 45.6)$$

so that $K = 0.371$, and the share of the inflation pressure carried by the first pair of plies

$= 0.371 \times 55.1 = 20.5$ pounds per square inch

and by the second pair of plies

$= 0.371 \times 50.1 = 18.6$ pounds per square inch

and by the third pair of plies

$= 0.371 \times 45.6 = 16.9$ pounds per square inch

Therefore, the pressure of the first pair of plies against the second pair $= 56-20.5 = 35.5$ pounds per square inch

and that of the second against the third

$= 35.5-18.6 = 16.9$ pounds per square inch

It is this pressure upon the carcass fabric that causes part of the frictional loss of power which accompanies flexure of the carcass in service.

Stresses Due to Deflection under Load

We are interested here not so much in the effect of the load upon the fabric stresses, as in the effect of the tire deflection due to the load, because the load itself does not produce any direct stresses in the carcass plies. Its effect is to alter the distribution of the fabric stresses already set up by the inflation pressure. It has already been shown that the fabric stress is proportional to the minor axis of the tire cross section. When the tire flattens due to an applied load this minor axis decreases, and the action relieves the deflected part of the carcass of some of the inflation stress. This stress relief is not equal to the load on the tire. It is the compressed air that sustains the load, and the stress relief in the fabric of the side walls is only a secondary effect. It can be proved that the ratio of load to stress relief is π (see appendix).

When a tire carcass is inflated all the fabric plies are subjected to tensile stress. There are no compressive stresses in the ply planes. Cotton fabric has a high and variable tensile modulus of elasticity, but a low compressive modulus. The result is that when the inflated carcass is flexed, the neutral line shifts from the median line of the carcass toward the region of increased tensile stress. This shifting of the neutral line causes a considerably greater reduction of tensile stress in the plies on the other side of the carcass than would occur in a material whose elastic properties obeyed Hooke's law. As the flexure increases the tensile stresses in these plies drop rapidly, and in cases of overloading, and, more particularly, underinflation, the tensile stress may completely vanish and the fabric begin to buckle. The experienced tire designer knows the danger of this condition, and protects the carcass against it by molding the tire carcass with such transverse curvatures as will cause minimum flexure under operating conditions.

The foregoing statements indicate in a general way the nature of the stress disturbance due to flexure. In order that the designer may determine where the danger lies and to what extent he must protect the tire carcass against it, he must be able to determine mathematically the true extent of the disturbance.

Stress Cycles—Fig. 3 shows the cross section of a tire on a rim, with the approximate location of the neutral axis of flexure of the carcass under inflation and load, shown by the dotted line. There are three different regions of tension, and three of compression—namely, at the tread, side wall, and bead. Figs. 4 to 9 represent roughly the cycles of strain to which the carcass in these three regions is subjected as the tire rolls along the road. "Normal fabric job" means the stress due to inflation pressure alone. In the tread region of the carcass the inner ply stress is never less than the normal fabric job, but increases as the deformation due to the load stretches the fabric on the inside. Fig. 4 shows the stress cycle to which this part of the carcass is subjected. On the outside the condition is different. The normal fabric job is the maximum tension sustained by the outer plies, so that the fabric stresses and strains decrease upon carcass deformation, as shown by Fig. 5. Figs 6 and 7 show the conditions at the side walls, and Figs. 8 and 9 at the bead. A carcass under

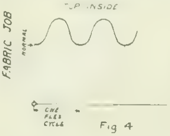

Fig 4

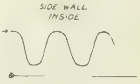

Fig 6

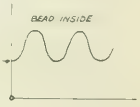

Fig 8

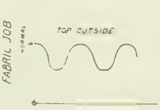

Fig 5

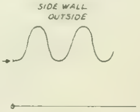

Fig 7

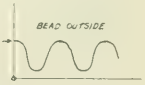

Fig 9

normal operating conditions does not fail by the action of any tensile stress so that failures in the regions indicated by Figs. 4, 7, and 8 are practically unknown. But the parts of the carcass in the compression regions on the inside of the side wall and the outside of the bead are more sensitive to abuse by the careless motorist. For a tire under normal inflation and normal loading, the amplitude of the stress cycles at these points is not great enough to extend into the compressive state. But underinflation or overloading upsets this nice balance. Underinflation alone moves all the curves downward into the trouble zone, because the normal fabric job is decreased, and the increased deflection of the carcass makes their amplitude greater. Overloading without underinflation increases the amplitude of the stress cycles, but does not affect the normal fabric job, so that, for abnormal tire deflections, the stress conditions in the fabric are probably less injurious with overloading as the cause than with underinflation.

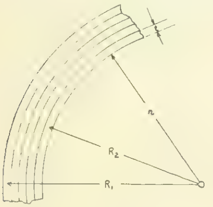

Fig 10

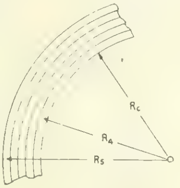

Fig 12

Critical Carcass Curvature—When a tire is flexed by a load, the minimum radius of curvature of the carcass cross section usually occurs at the lower side wall, not far from the edge of the tread. It is at this point where the carcass first develops critical curvature, or curvature for which there is no stress on the inner ply. Beyond this curvature the fabric buckles. Fig. 10 represents this part of the uninflated cross section of a tire.

Let r = internal radius of the unstressed carcass
R_1 = radius to center of outer ply of unstressed carcass
R_2 = radius to center of inner ply of unstressed carcass
T = ply thickness
N = number of plies

Then $$R_1 = r + T(N - {}^1/_2) \qquad (24)$$

$$R_2 = r + \frac{T}{2} \qquad (25)$$

Let F_3 = average inflation stress per ply per unit width

This stress is obtained from Equation 9 by substituting for D_T a new value of D_T decreased by the amount of the tire deflection due to the load. This load should be taken as the maximum load to which the tire may be frequently subjected. Its value may be taken in any specific instance as equal to twice normal load. This will cover the usual abnormal tire deflections due to overloading, vertical bounding, and the effect of centrifugal force on the car when turning.

Then the total carcass stress per unit width due to inflation

$$= NF_3 \qquad (26)$$

Now, suppose the part of the carcass under consideration to be deflected to the critical curvature, so that there is no stress on a certain sector of the inner ply, and all the stress due to inflation is sustained at that point by the outer plies. The strain values in the consecutive plies must always form an arithmetical series. The effect of shearing strains is not considered in this analysis.

Let Fig. 11 represent the elasticity curve for the fabric, and let AB, AC, AD, and AE represent the strains in consecutive plies, for the critical condition of no strain in the first (or inner ply) of the carcass. Then BF, CG, DH, and EK represent the respective stresses in these plies. With constant inflation, the total carcass stress NF_3 must always be equal to

$$BF + CG + DH + EK \qquad (27)$$

Since the fabric stress does not bear any simple relation to the fabric strain, it is necessary to determine the ply stresses by this graphical method.

Let E_0 = elongation AE of the outer ply
R_3 = imaginary value of radius R_1 corresponding to stress EK per ply, for the unflexed carcass

Fig. 12 represents the tire carcass flexed to critical internal radius of curvature R_c.

Now $$R_3 = R_1(1 + E_0) \qquad (28)$$

$$R_4 = R_5 - T(N-1) \qquad (29)$$

$$\frac{R_5}{R_4} = \frac{R_3}{R_2} \qquad (30)$$

Transposing, $$R_5 = \frac{R_4 R_3}{R_2}$$

and substituting the value of R_3 from Equation 28 and of R_2 from Equation 25

$$R_5 = \frac{R_1 R_1 (1 + E_0)}{r + \frac{T}{2}} \qquad (31)$$

Substituting this value of R_5 in Equation 29

$$R_4 = \frac{R_4 R_1 (1 + E_0)}{r + \frac{T}{2}} - T(N-1) \qquad (32)$$

and substituting the value of R_1 from Equation 24

$$R_4 = R_4(1 + E_0)\left[\frac{r + T(N-1)}{r + \frac{T}{2}}\right] - T(N-1) \qquad (33)$$

Dividing through by R_4

$$1 = (1 + E_0)\left[\frac{r + T(N-1)}{r + \frac{T}{2}}\right] - \frac{T(N-1)}{R_4}$$

Therefore, $$\frac{T(N-1)}{R_4} = \frac{(1 + E_0)[r + T(N-1)] - \left(r + \frac{T}{2}\right)}{r + \frac{T}{2}}$$

$$R_4 = \frac{T(N-1)\left(r + \frac{T}{2}\right)}{(1 + E_0)[r + T(N-1)] - \left(r + \frac{T}{2}\right)} \qquad (34)$$

and the critical radius $R_1 = R_4 - \frac{T}{2}$

$$R_c = \frac{T(N-1)\left(r + \frac{T}{2}\right)}{(1 + E_0)[r + T(N-1)] - \left(r + \frac{T}{2}\right)} - \frac{T}{2} \qquad (35)$$

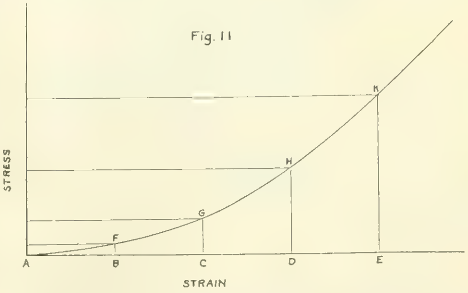

Fig. 11

The less the value of R_c, the greater will be the safety for the carcass. Obviously, its value for any tire should be less than the internal radius of the carcass under the extreme deflection.

CARCASS SHEARING STRAINS—If the calculation of critical curvature by Equation 35 yields a value below any carcass radius to which the tire would be frequently subjected, it is not necessary to consider the modifying effect of skim-coat shears. Carcass shear diminishes the value of critical radius by allowing the fabric to move away from the zone of compression.

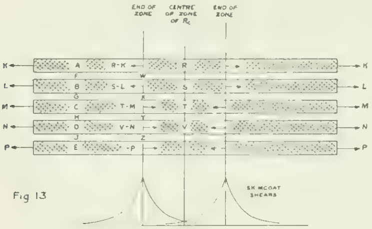

Fig 13

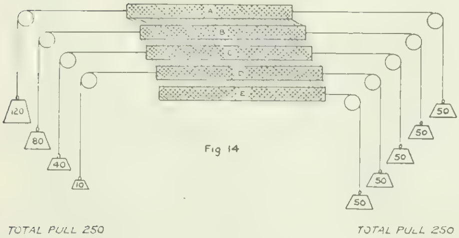

Fig 14

Let Fig. 13 represent the developed transverse cross section of a tire in the region of critical curvature R_c. Let A, B, C, D, and E represent the carcass plies separated by the rubber skim coats F, G, H, and J, respectively. Equation 23 enables us to calculate the fabric stress in each ply of the unflexed carcass. For the purpose of this shear analysis, the term $\frac{1}{2\sin {}^2\Theta} \times \frac{\sin 2\Theta}{\sin 2B}$ must be omitted in order to obtain the ply stress parallel to the plane of the tire cross section, and not in the direction of the threads. It is assumed that these ply stresses per unit of tire circumference at the center of the zone of R_c have been calculated and found to be K, L, M, N, and P, respectively. Now let a portion of the carcass cross section be flexed to critical radius R_c. Then the stress P on the inner ply becomes zero at the center of the zone of R_c, so that the stresses R, S, T, and V in the remaining plies must be equal in total value to $K + L + M + N + P$ (see Equation 27). In Ply A there is a change of stress of $R-K$, acting away from the center of the zone of R_c.

In Ply B, the change of stress is $S - L$
Ply C, the change of stress is $T - M$
Ply D, the change of stress is $V - N$
Ply E, the change of stress is $- P$

These changes in ply stresses are produced by the components of the skim-coat shear stresses resolved along the planes of the fabric plies, so that the total shear stress W in the skim coat between Plies A and B measured in either direction from the center of the zone of R_c

$$= R-K \tag{36}$$

the shear stress X in skim coat G

$$= (R-K) + (S-L) \tag{37}$$

the shear stress Y in skim coat H

$$= (R-K) + (S-L) + (T-M) \tag{38}$$

the shear stress Z in skim coat J

$$= (R-K) + (S-L) + (T-M) + (V-N) \tag{39}$$

The intensity of shear stress is at a maximum at the point of maximum rate of change of carcass radius, which occurs at the edge of the zone of R_c, and from this point its value dies away logarithmically in both directions—that is, its rate of change is equal to its actual value at any point.[4] This is shown by the curves in Fig. 13, or expressed mathematically:

Let F_s = maximum shear force between any two plies
F_x = shear force at point distant X from maximum shear point
e = base of natural logarithms

Then
$$F_x = F_s e^{-x} \tag{40}$$

The rate of change[4] of the shear force F_x

$$= \frac{d}{dx} F_s e^{-x} = -F_s e^{-x} \tag{41}$$

The total[5] shear force W, or X, or Y, or Z

$$\begin{aligned} &= 2\int F_x dx = 2\int F_s e^{-x} dx = 2\left[1 - F_s e^{-x}\right]_0^{\alpha} \\ &= 2F_s \end{aligned} \tag{42}$$

Therefore, the maximum intensity of shear force is equal in value to one-half the total shear force, and its location is at the edge of the zone of R_c, the point of maximum rate of change of carcass curvature. Its value is not a function of the skim-coat thickness.

It is now necessary to determine the amount of interference of the shear stresses with the critical radius of carcass curvature at the center of the zone of R_c.

Considering the carcass as a whole, the total of all the shear forces at the edge of the zone of R_c

$$= \frac{W + X + Y + Z}{2} \tag{43}$$

Individually, they die away logarithmically, so therefore collectively they do the same. Thus, their imaginary collective value F_x at the center of the zone of R_c, where $X = \frac{\phi}{2}\left(R_c + \frac{NT}{2}\right)$,

is equal to
$$\frac{W + X + Y + Z}{2} e^{-\frac{\phi}{2}\left(R_c + \frac{NT}{2}\right)} \tag{44}$$

where ϕ = angle subtended by zone of R_c

The real value of this collective shear must be zero, because there can be no transference of shear force through the center of the zone of R_c in this symmetrically flexed carcass, so that the value calculated above of shear force F_x is imaginary, and represents only the tendency of the shear forces to affect the tension distribution between the fabric plies.

Since we assumed primarily that this zone of the carcass was flexed to critical curvature, the shear force F_x can have no real effect upon the tensions in the various plies. Its tendency to increase the tension on the inner plies causes the final value of critical radius to be less than it would be had there been no shear forces present, so that the shear forces afford a protection to the fabric, but create fatiguing strains in the skim coats. The integral value of the uncompleted decay of the shear forces, which are apparently suddenly cut off at the center of the zone of R_c, does not vanish and reduce the value of the total shear forces W, X, Y, and Z. These forces remain as calculated in Equations 36 to 39, and the amount that is lost through the uncompleted decay is made up by the production of a transition spiral between the R_c zone and the unflexed part of the carcass. Undoubtedly, this spiral has a modifying effect upon the maximum value of shear.

Continuing the mathematical analysis, the imaginary value of shear force in skim coat Z at the center of the zone of R_c

$$= \frac{ZF_x}{W + X + Y + Z} \tag{45}$$

By referring to the fabric elasticity curve in Fig. 11, we can obtain the fabric strain E_i corresponding to the imaginary stress on the inner ply as given by Equation 45.

All the data necessary to calculate the new value of critical radius R_c have now been obtained.

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[4] Murray, "Differential and Integral Calculus," **1908**, p. 65, Note **3**.

[5] Murray, "Differential and Integral Calculus," **1908**, p. 293.

Let R_6 = carcass radius to center of inner ply
R_7 = carcass radius to center of outer ply

Then
$$\frac{R_7}{R_6} = \frac{R_5}{R_4(1-E_i)} \tag{46}$$

But
$$R_7 = R_6 + T(N-1)$$
$$R_5 = R_4 + T(N-1)$$

Therefore,
$$\frac{R_6 + T(N-1)}{R_6} = \frac{R_4 + T(N-1)}{R_4(1-E_i)}$$

simplifying
$$1 + \frac{T(N-1)}{R_6} = \frac{1}{1-E_i} + \frac{T(N-1)}{R_4(1-E_i)}$$
$$\frac{T(N-1)}{R_6} = \frac{T(N-1)}{R_4(1-E_i)} + \frac{E_i}{1-E_i}$$
$$= \frac{T(N-1) + E_iR_4}{R_4(1-E_i)}$$

Therefore,
$$R_6 = \frac{TR_4(N-1)(1-E_i)}{T(N-1) + E_iR_4}$$

and the new critical radius $R_c = R_6 - \frac{T}{2}$

$$R_c = \frac{TR_4(N-1)(1-E_i)}{T(N-1) + E_iR_4} - \frac{T}{2} \tag{47}$$

The value of R_4 has already been calculated (see Equation 34).

The foregoing analysis represents the simplest case of a flexed carcass, in which the carcass curvature on either side of the zone of critical curvature is equal to the original molded curvature. In this case there is no interference of other zones of curvature change.

Fig. 14 presents a diagrammatic picture of the ply stress conditions in the critically flexed carcass. The weights on the right side represent the uniform ply tensions outside of the zone of flexure, and those on the left the unbalanced ply stress conditions due to flexure. The sum total of all the weights in each case is the same, and represents the inflation stress acting on the carcass.

In order that we may get a better conception of the relative values of critical curvatures as calculated by Equations 35 and 47, let us consider the special case of a 5-ply square-woven fabric tire, of ply thickness 0.040 inch and internal carcass radius 1.5 inches. Assuming that the fabric stretch E_o is 8 per cent, we would find the critical carcass curvature, as calculated by Equation 35, which neglects the action of skim-coat shears, to be 0.88 inch. Calculating the critical curvature by Equation 47, which takes skim-coat shear into consideration, and assuming the zone of R_c to be 2 inches wide, we would find a critical curvature of 0.79 inch. The difference between the two values indicates the extent to which shear reduces the fabric fatigue.

The effect upon the fabric stresses in a whole tire carcass under the combined action of flexure and shear is, however, more complex than the simple case analyzed above, but an accurate determination can be made by elaborating upon the fundamental analysis. It becomes necessary to make a "shear survey" of the whole tire carcass. If the designer's objective is the design of a completely new tire, it is necessary for him to get his conception of the whole problem by making shear surveys upon some tires already manufactured. This can be done by taking measurements upon the tire under all the required conditions—viz., molded, inflated, and loaded—and under any abnormal conditions that the designer may deem necessary. The measurements may be made by dimension scaling, or by taking plaster casts of the outside of the tire, or of the inside. The writer cannot go into the details of this work here, but when once the principles of the work are clearly fixed the methods may easily be planned. The designer must remember, however, that the carcass curvatures are functions of many variables, chief of which are fabric angle, ratio of extreme to cross-sectional tire diameter, tread radius, and cross-sectional disposition of tread-stock. For the latter two reasons tread design is closely related to carcass stress analysis.

Fig. 15 represents a typical curvature analysis for a tire carcass. The abscissas represent displacement along the neutral axis of the carcass from the point opposite the center of the tread to the rim contact point. The ordinates represent the curvature changes under the given conditions of inflation and load.

Let r_o = original carcass radius of curvature
r_x = deflected radius at any point X

$$\text{Then the change of curvature} = \frac{1}{r_x} - \frac{1}{r_o} \tag{48}$$

The curvature changes in the tread and bead regions are negative, and at the side walls positive.

The maximum change of curvature occurs in the region AB. Its value is AF. Were it not for the disturbing effect of the unsymmetrical shears at either end of this region, the maximum shift of the neutral axis of the carcass would occur at the point C, midway between the points A and B. But owing to these unsymmetrical shears, the point is shifted to G, at which point the two shears neutralize each other, as shown by the intersection of curves HK and LM, representing the logarithmic decrement loci of the shears AD and BE. The distribution of the total carcass stress among the plies may now be determined by a method similar to that by which the critical curvature was previously calculated, allowance being made for the effect of shear.

In order that the reader may get some idea of the extent to which the designed cross-sectional shape of a tire may affect the carcass tension and shear stresses under inflation and load, Figs. 16, 17, and 18 have been drawn to represent diagrammatically the stress conditions corresponding to different molded shapes. The weight marked "Inflation" suspended over the pulley represents the way in which the inflation stress acts on the carcass, and the weight marked "Load," the way in which the load acts upon the flexed part of the tire. Contemporary tires of recent manufacture yield examples of all three classes, which erroneously leads the casual observer to believe that molded shape means little. Molded shape is but one factor in tire design, and the off-shape tire may survive present competition because it possesses good qualities from other standpoints. But it will never be a super-mileage tire, because it possesses inherent weakness.

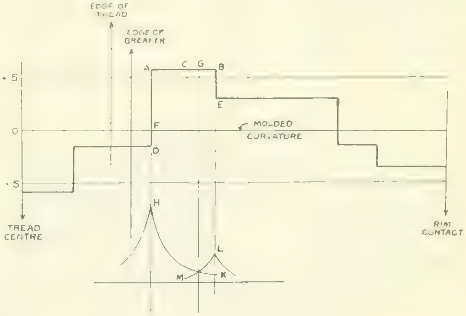

Fig 15

Skim-Coat Shear Strains—This subject is so closely connected with fabric stress analysis that the method of calculating the value of maximum shear strain will be given. It has been calculated that the maximum intensity of shear force F_s is equal to one-half of the total shear force (Equation 42).

Let M_s = skim-coat modulus of elasticity up to the usual skim-coat strain
ω = angular shear of skim coat

Then $F_s = M_s\,(\sec\omega - 1)\sin\omega \quad (49)$

$= M_s\,(\tan\omega - \sin\omega) \quad (50)$

From Equation 50 the shear angle can be calculated, and the skim-coat elongation $= \sec\omega - 1 \quad (51)$

In the absence of definite data on fatigue of the bond between the skim-coat rubber and the fabric, the designer must base his critical values upon the calculated skim-coat elongations in tires which have established a known performance.

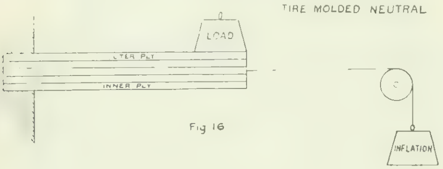

Fig 16

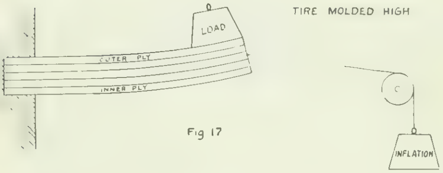

Fig 17

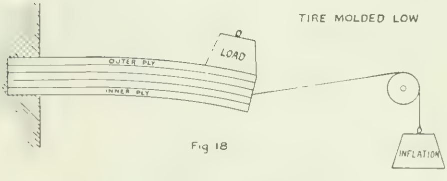

Fig 18

DYNAMIC STRESSES

TRACTION AND BRAKING STRESSES—The tires on the driving wheels of a car are subjected, in addition to the stresses due to inflation and load, to the reciprocating stresses of traction and braking. Since tires are built for universal service on idling or driving wheels, these stresses become a factor in all pneumatic tire design.

The maximum rate of change of velocity of a car occurs when the brakes are strongly applied. The rate of retardation may be carried to the skidding point of the tire on the road surface. At this point the retarding force acting on the tire is equal to the product of the weight sustained by the tire and the coefficient of friction between the tire and the road surface. This coefficient may have a maximum value as large as unity. The actual weight supported by the rear tires when braking the car is decreased by the tendency of the car to overturn forward, similar to the tendency to overturn sidewise when turning a corner. Therefore, the virtual coefficient of friction based on the weight sustained by the tire at rest or in uniform motion will be less than its actual value based on the real weight supported when braking. The reverse effect takes place when the speed of the car is accelerated. The inertia of the car causes a tendency to overturn backward, and extra weight is thrown on the rear wheels, so that cars with short wheel-bases assume that peculiar crouching attitude when started suddenly. The value of the virtual coefficient of friction in this case is greater than its actual value.

Let W = standard recommended loading for the tire
μ = virtual coefficient of friction between tire and road surface

Then the maximum accelerating or braking force F_M on the tire $= W\mu \quad (52)$

If the rate of acceleration or deceleration is known and it is required to find the corresponding force F_N acting on the tires
let a = rate of acceleration or deceleration
W_c = car weight
g = acceleration due to gravity

$$\text{Then } F_N = \frac{W_c a}{2g} \qquad (53)$$

If the car speed and the power transmitted by the engine to the tires are known, the tractive force F_T per tire can be calculated.

Let V = car velocity in miles per hour

$$\text{Then the tractive force } F_T \text{ per tire} = \frac{187.5 \text{ h. p.}}{V} \qquad (54)$$

If a car ascends a grade of G per cent at uniform speed, the

$$\text{tractive force } F_G \text{ per tire} = \frac{W_c G}{200} \qquad (55)$$

and must be added to the tractive force F_T to obtain the total force upon the tire.

From these equations we can determine the values of this class of dynamic stresses under various conditions of performance on the road. It is necessary to assure sufficient protection to the carcass to withstand, not only the greatest of these stresses, but also the fatiguing action of all of them. Having determined their numerical values, it is then necessary to know the shape and size of the area of contact between the tire and the road surface.

Let the ellipse in Fig. 19 represent the contact area between the tire and the road. It is approximately elliptical in shape, the major axis being parallel to the direction of motion of the tire. Neglecting shear displacement in the rubber, the traction or braking force is transmitted uniformly to every unit area of fabric lying directly over the road contact area. Let OA and OB represent the two directions of the fabric threads in the carcass. By drawing CD and EF parallel to OA and tangent to the road contact ellipse, we obtain the zone of fabric threads lying parallel to OA that are affected by the stresses under consideration. By drawing two similar lines parallel to OB, we obtain the other zone of fabric threads similarly affected. The line GH represents the length of extended major axis intercepted by these parallel lines. To obtain the maximum force per unit width of fabric, it is necessary to take two points on the major axis unit distance apart, and equidistant from the point O, and draw two lines, KL and MN, through these points and parallel to OA.

The stress intensity per unit area of road contact ellipse

$$= \frac{F_M}{A_E} \qquad (56)$$

where A_E = area of road contact ellipse

Therefore, the stress acting on the area A_M between the lines

$$KL \text{ and } MN \quad = \frac{A_M F_M}{A_E} \qquad (57)$$

Resolving this stress along the direction of the fabric threads, we get the stress intensity per unit width of carcass

$$= \frac{A_M F_M}{2A_E \sin\Theta\cos\Theta} \qquad (58)$$

Dividing the stress equally among the carcass plies, and correcting for fabric distortion, we get the stress F_D per unit of original width of fabric

$$= \frac{A_M F_M}{2NA_E \sin\Theta\cos\Theta} \times \frac{\sin 2\Theta}{\sin 2B} \qquad (59)$$

But $\quad \sin 2\Theta = 2\sin\Theta\cos\Theta$

$$\text{Therefore,} \quad F_D = \frac{A_M F_M}{NA_E \sin 2B} \qquad (60)$$

For F_M we may substitute F_N, F_T or F_G according to the conditions under which we wish to calculate the dynamic stress in the fabric. This equation shows that the fabric stress is independent of the stretch applied to the fabric in building the carcass.

Let us, for example, calculate the maximum fabric stress at the edge of the road contact ellipse in a 33 x 4 S. S. cord tire, when the brakes are strongly applied.

Let $W = 850$ pounds
$\mu = 1.0$
Then $F_M = 850 \times 1.0 = 850$ pounds (Equation 52)
Let the stress on area $A_M = 150$ pounds (Equation 57)
$N = 3$, and $B = 45°$

$$\text{Then the fabric stress} = \frac{150}{3 \times \sin 90°} \text{ (Equation 60)}$$
$$= 50 \text{ pounds per inch width}$$

Every part of the tire carcass, as it revolves on the wheel and makes contact with the road surface, is subjected to the simultaneous action of the dynamic stress of traction or braking and the stress due to flexure under load. The latter stress may be determined by the method of calculation outlined under "Stresses Due to Deflection under Load." This stress is at a maximum in the outer ply of the carcass, and has a value EK (Equation 27), so that the maximum fabric stress due to these two simultaneous stresses is equal to the sum of the two stresses.

CENTRIFUGAL STRESSES

Centrifugal stress is generated in a tire owing to the action of its mass, which tends to pull away from the center about which the tire revolves. It is a function of the mass of the tire, of the extreme diameter, and of the speed at which the tire revolves. Its value is a minimum in that part of the carcass directly under the center of the tread, and is cumulative toward the bead region. Therefore, in a straight-side tire the bead wires must finally supply the total reaction to this force.

The centrifugal force acts in a direction parallel to the minor axis of the cross-sectional ellipse, and hence increases this minor axis. Its action has the characteristic of a directional inflation pressure away from the center of rotation of the tire, and thus it decreases the deflection of a tire when the latter revolves on the road.

The total mass of a tire is made up of (1) casing, (2) inner tube, (3) compressed air, and (4) flap (if used). In calculating the centrifugal stress which the bead must resist, all these parts must be taken into consideration; in other cases only part is taken, depending upon the location of the point at which the stress is to be determined.

The elementary equation of centrifugal force is

$$F_c = \frac{Wv^2}{gR} \qquad (61)$$

where F_c = centrifugal force
W = weight of the body
v = linear velocity
g = acceleration due to gravity
R = radius of rotation to center of gravity of body

Adapting this equation to the conditions in a tire, let Fig. 3 represent the tire cross section and $X-X$ the point at which we wish to determine the centrifugal ply stress.

Let W_s = weight of tire above lines $X-X$
W_T = weight of tube lying between lines parallel to the minor axis of cross-sectional ellipse, and passing through the points O, the intersection points of the lines $X-X$ and the neutral axis of the carcass
W_A = weight of air between these lines
W_F = weight of flap between these lines

Then the total mass M_T, which generates the centrifugal force imposed upon the tire at the zone $X-X$, is

$$M_T = \frac{W_s + W_T + W_A + W_F}{g} \qquad (62)$$

Let R_G = radius of gyration of this total mass
Then the moment of inertia I of the mass M_T is

$$I = M_T R_G^2 \qquad (63)$$

and the centrifugal force becomes

$$F_c = \frac{I}{R_G} (2\pi \text{ r. p. s.})^2 \qquad (64)$$

where r. p. s. = speed of tire in revolutions per second

If the tire speed is calculated from the speed of the car on the road, allowance must be made for the decreased tire diameter at the road contact surface, and if the tire on the driving wheel is under consideration a correction must be made for the relative slip between the tire and the road surface due to the effect of traction.

The total centrifugal force F_c having been determined, its intensity per unit width of carcass ply must be found. Referring to Fig. 3, it will be seen that the force F_c is distributed over two circumferential zones $X-X$, one on each side of the tire.

Let R_x = radius of revolution of point O
Then the total width of carcass fabric over which the force F_c is distributed is

$$4\pi N R_x \qquad (65)$$

If A = angle between minor axis of cross-sectional ellipse and the tangent to ellipse at intersection point O of line $X-X$

then the centrifugal stress intensity per unit width of carcass ply becomes

$$\frac{F_c}{4\pi N R_x \cos A} \qquad (66)$$

Expressing this stress intensity in terms of stress per unit of original fabric width, the fabric stress S_c becomes

$$S_c = \frac{F_c}{4\pi N R_x \cos A} \times \frac{1}{2 \sin^2 \Theta} \times \frac{\sin 2\Theta}{\sin 2B} \qquad (67)$$

The effect of this stress need not be considered in connection with inflation and deflection stresses, because its action is considerably reduced at that part of the tire in contact with the road. It is of importance principally in the calculation of bead wire stress, and for its effect upon the dynamic tire deflection.

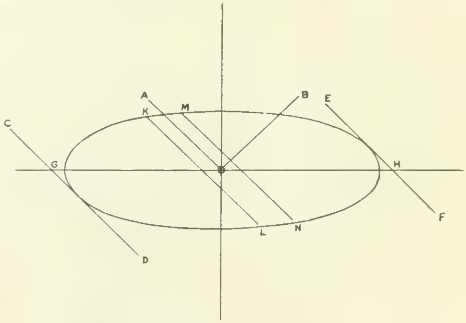

Fig. 19

The centrifugal force may be expressed in terms of equivalent inflation pressure as follows:

Calculating the centrifugal force F_c for the mass of the tire, tube, flap, and air, but excluding the bead wires, and distributing this force over the plane generated by the rotation of the major axis of the cross-sectional ellipse about the axis of rotation of the tire, we get the equivalent inflation pressure P.

$$P_c = \frac{F_c}{\pi D_R d} \qquad (68)$$

This virtual inflation pressure will decrease the tire deflection relative to the road surface by the same amount as an actual pressure increase above the normal inflation pressure.[6] It does not necessarily decrease the fatigue in the carcass. The centrifugal force elongates the minor axis of the cross-sectional ellipse in the part of the carcass not in contact with the road by approximately the same amount as it increases this axis in the road contact region, so that the total variation in length of the minor axis per cycle is not appreciably changed.

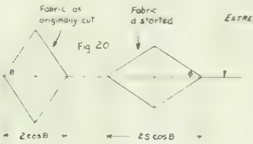

Fig 20

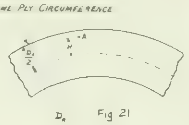

Fig 21

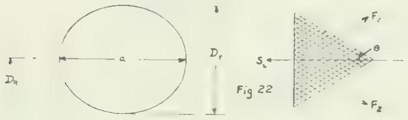

Fig 22

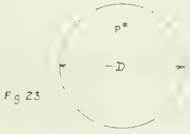

Fig 23

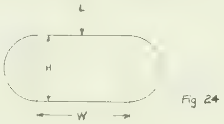

Fig 24

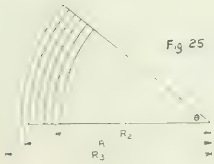

Fig 25

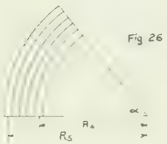

Fig 26

Indeterminate Stresses—The most important case in this class of stresses is that due to contact of the tire with a sharp object on the road, causing severe reverse flexure of the carcass, and often causing that injury known as stone-bruising, or fracture of the inner ply. The contact is so sudden and of such short duration that the tire has no time to rebound from the impact, so that the tire suffers a definite deformation. The extreme effect of this sharp carcass flexure is to throw the whole inflation stress in the carcass on the inner ply only. It is therefore important to so design a tire that the ultimate tensile strength of the fabric is in excess of the inflation stress multiplied by the number of carcass plies; or conversely, that the stress due to inflation pressure is made less than the ultimate tensile strength of the fabric divided by the number of plies. The rigidity of the carcass adds somewhat to the stress on the inner ply during flexure, so that the safety factor should not be shaded too closely to the critical value.

Appendix

Proof of Equation 4 in Detail—When the tube is inflated to fill the interior of the tire carcass, the outer surface of the tube coincides with the inner surface of the carcass. Therefore, the external cross-sectional perimeter L_T of the tube is stretched until it equals the internal cross-sectional perimeter L_c of the carcass, so that the strain per unit of transverse perimeter of tube equals

$$\frac{L_c-L_T}{L_T}$$

and if m equals the ratio of stress to strain per unit cross-sectional area of tube stock corresponding to the strain of complete inflation of the tube, then the force per unit of tube length resisting the inflation pressure equals the elastic modulus of the stock times the cross-sectional area of tube times the strain per unit of transverse perimeter. Represented symbolically, this force equals

$$mt\,\frac{L_c-L_T}{L_T} \tag{69}$$

Let P_T = air pressure required to inflate the tube to fill the interior of the carcass

Then, according to Equation 1, the transverse stress per inch of tube length

$$= \frac{P_T \times \text{tube cross-sectional inflated diameter}}{2} = \frac{P_T}{2}\,\frac{L_c}{\pi} \tag{70}$$

and equating the expressions 69 and 70, which represent the same force in different terms,

$$\frac{P_T L_c}{2\pi} = mt\,\frac{L_c-L_T}{L_T}$$

and transposed

$$P_T = 2\pi\, mt\,\frac{L_c-L_T}{L_c L_T}$$

Proof of Equation 12—Fig. 20 represents the fabric parallelograms referred to in connection with Equation 10. The sides of these parallelograms are all equal, because the distortion alters only the internal angles.

Let S = ratio of stretched to unstretched length of the fabric ply at the extreme ply diameter.

Then it may readily be seen by referring to Fig. 20 that the relation of the fabric angle Θ to the bias angle B is

$$\cos\Theta = S\cos B \tag{71}$$

This relation holds true only at the extreme ply circumference. To establish this relation at any other point on the carcass, the fabric distortion at that point must be considered. The stretch of the fabric ply at any point (such as at A in Fig. 21) to conform to the shape of the core upon which the tire is built is proportional to the distance of the point from the center of rotation of the core, so that if S is the circumferential fabric distortion at the extreme ply diameter, then the circumferential distortion at the point A is

$$S\,\frac{D_R+2H}{D_R+D_T} \tag{72}$$

Equation 71 thus generalized becomes

$$\cos\Theta = S\cos B\left(\frac{D_R+2H}{D_R+D_T}\right)$$

Proof of Equation 13—The ellipse in Fig. 22 represents the cross-sectional median line of a tire carcass.

Let a = major axis of ellipse
D_T = minor axis of ellipse

Then the area of the cross-sectional ellipse

$$= \frac{\pi}{4}\,aD_T \tag{73}$$

and the force tending to elongate the carcass

$$= (P-P_T)\,\frac{\pi}{4}\,aD_T \tag{74}$$

This force acts over whole perimeter of the carcass cross section. The length of the perimeter of the cross-sectional ellipse

$$= \pi\sqrt{aD_T} \tag{75}$$

Therefore, the longitudinal stress S_L per unit of perimeter

$$= \frac{(P-P_T)\,\frac{\pi}{4}\,aD_T}{\pi\sqrt{aD_T}}$$

$$= \frac{(P-P_T)\sqrt{aD_T}}{4} \tag{76}$$

This stress is distributed among all the plies of the carcass, so that the stress per ply in one direction

$$= \frac{(P-P_T)\sqrt{aD_T}}{8N} \tag{77}$$

Resolving this stress along the direction of the threads, we obtain the stress per unit width of fabric measured perpendicularly to the threads of

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[6] *J. Soc. Automotive Eng.*, **11**, 438 (1922)

$$\frac{(P-P_T)}{8N}\sqrt{aD_T}\sec{}^2\Theta \qquad (78)$$

and correcting for the thread concentration due to fabric distortion, we get the real fabric stress

$$F_2 = \frac{(P-P_T)}{8N}\sqrt{aD_T}\sec{}^2\Theta\,\frac{\sin 2\Theta}{\sin 2B}$$

Proof of Load Relation to Fabric Stress Relief—Fig. 23 represents diagrammatically the cross section of an inflated carcass, having a diameter D and an inflation pressure P.

According to Equation 1, the transverse fabric stress $= \frac{PD}{2}$.

Fig. 24 represents the same carcass deflected under the load L per unit of carcass length.

$$\text{The new fabric stress} = \frac{PH}{2} \qquad (79)$$

$$\text{So that the stress relief due to flexure} = \frac{PD}{2} - \frac{PH}{2} \qquad (80)$$

$$= \frac{P}{2}(D-H) \qquad (81)$$

Now, because the carcass retains the same transverse perimeter

$$2W = \pi D - \pi H \qquad (82)$$

$$= \pi(D-H)$$

$$\text{or } W = \frac{\pi}{2}(D-H)$$

$$\text{But } W = \frac{L}{P} \qquad (83)$$

$$\text{So that } L = \frac{\pi P}{2}(D-H)$$

Therefore, the ratio of load to stress relief

$$= \frac{\frac{\pi P}{2}(D-H)}{\frac{P}{2}(D-H)} \qquad (84)$$

$$= \pi$$

Proof of Equation 30 that $\frac{R_5}{R_4} = \frac{R_3}{R_2}$—Fig. 25 represents a sector of unstressed carcass subtended by the angle Θ.

R_1 = radius to center of outer ply

R_2 = radius to center of inner ply

R_3 = imaginary value of radius R_1, if the tire were simply inflated until the stress per ply were equal to that sustained by the outer ply under critical curvature conditions. (This has already been explained in the text. See Equation 27.)

Now let Fig. 26 represent the same sector of carcass flexed to critical curvature. The subtended angle α is greater than the angle Θ.

Since the stress on the outer ply is the same in both Figs. 25 and 26, then the outer ply lengths are the same, so that

$$R_3\Theta = R_5\alpha \qquad (85)$$

Similarly, the inner ply lengths are the same, so that

$$R_2\Theta = R_4\alpha \qquad (86)$$

Therefore, combining Equations 85 and 86

$$\frac{R_5\alpha}{R_4\alpha} = \frac{R_3\Theta}{R_2\Theta} \qquad (87)$$

and simplifying

$$\frac{R_5}{R_4} = \frac{R_3}{R_2} \qquad (88)$$

The World's Dairy Congress

An International Congress on dairying, held in this country October 2 to 10, was attended by 1800 delegates, including over 200 from 43 foreign countries.

At the opening sessions in Washington, October 2 and 3, the delegates were welcomed by Secretary Hughes and addresses were made by Secretaries Wallace and Hoover. Additional sessions were devoted to papers on international trade and the development of the dairy industry. On October 4 the Congress adjourned to Philadelphia, where a demonstration was given of the methods used by the National Dairy Council in educating the public to the nutritive value of milk. From Philadelphia special trains took the delegates to Syracuse, where the National Dairy Exposition was held. October 5, 6, 8, 9, and 10 were given over to technical papers on topics related to the dairy industry.

About 245 papers were presented at the 27 sessions into which the Congress was divided. Abstracts of the papers in English, French, German, and Spanish were available at registration, and full papers and proceedings will be published by the Government. Three of the sessions were devoted to the nutritional side of the milk question, and included papers by McCollum, Mendel, Blackham, Sherman, Block, and Pirquet. R. M. Allen and Chas. A. Glabau discussed the question of the use of milk and milk powders in the baking industry, both from the standpoint of the increase in nutritive value and the effect of the addition of milk solids on the size and quality of the loaf. In the section on equipment two papers discussed the use of various metals in the handling of milk and the manufacture of milk products.

In the session devoted to the transportation of milk considerable attention was given to the use of steel tanks for both automobile and railroad shipments. A collection of papers on milk secretion and the nutrition of dairy cows included contributions by Porcher, Isaachsen, Koestler, Forbes, and Meigs. H. M. Evans discussed the occurrence and distribution of a new dietary factor essential to reproduction.

Additional papers of interest to chemists appeared in various sessions of the Congress. These included a paper by L. L. Van Slyke on "The Chemistry of Casein;" by L. S. Palmer on the "Chemistry of Milk and Milk Products from a Colloidal Standpoint;" by Alan Leighton and P. N. Peter on "Factors Influencing the Crystallization of Lactose;" by A. Miyawaki on "The Keeping Quality of Sweetened Condensed Milk;" by H. H. Somer on "The Heat of Coagulation of Milk;" by A. Leighton and E. F. Deysher on "Factors Influencing the Heat Coagulation of Milk and the Thickening of Condensed Milk;" by G. C. Supplee on "The Keeping Quality of Dry Milk;" by G. E. Holm and G. R. Greenbank on "The Keeping Quality of Butterfat with Special Reference to Milk Powder;" and by H. Jephcott and N. Ratcliffe on "Fat in Commercial Casein." The splendid program was largely due to the work of L. A. Rogers, of the Dairy Division, U. S. Department of Agriculture.

Syracuse University at a special convocation conferred the degree of doctor of science on C. J. Hastings, of Canada; C. Orla-Jensen, of Denmark; Masayoshi Sato, of Japan; Haakon Isaachsen, of Norway; Gerald Leighton, of Scotland; Robert Burri, of Switzerland; Robert Stenhouse Williams, of England; Charles Borcher, of France; and Sir Arnold Theiler, of South Africa. The degree of doctor of laws was conferred on Cesares Longobardi, of Italy, and H. E. Van Norman, president of the Congress.

A number of excursions were arranged for the delegates, both before and following the Congress, to farms, dairy manufacturing establishments, and educational institutions. These included an automobile trip ending at Ithaca for the dedication of the new dairy building of Cornell University and a long trip to the Pacific Coast.

The Absorption of War Gases by Rubber and Rubberized Fabric[1]

By Thomas M. Rector

14 Church St., New York, N. Y.

Soon after the adoption of the Akron Tissot and Kops Tissot face pieces for the American gas mask, Major R. G. Pierce, of the Physiological Division of the Chemical Warfare Service, made the discovery that practically every face piece of these types, no matter how well fitted, leaked air in measurable amounts. The amount of "leak-in" varied from a few cubic centimeters of air per minute to several hundred per minute. This discovery caused a great deal of controversy in the chemical warfare laboratories. Those who doubted that the face pieces leaked, immediately raised the question: "Why aren't the men gassed if the face pieces leak?"

The investigations reported in this paper were made for the purpose of answering this question. The results of the experiments are reported at this time more on account of the unique methods employed and their possible utilization in other fields, than for their bearing on gas-mask development.

CHLOROPICRIN IN AIR

Clean-cut practical methods were available for all the common war gases when present in amounts exceeding 25 parts per million of air. Below this concentration no chemical method could be depended upon. Chloropicrin, when present in amounts exceeding 2 parts per million in air causes involuntary closing of the average eye. It was noted, however, that a measurable interval of time elapsed between exposure to the gas and the closing of the eye. Further tests showed that this time interval varied sharply with the concentration of the gas, and that this variation could be used to determine chloropicrin concentration between 1 part per million and 30 parts per million with enough accuracy for the purpose of the investigation.

Using these facts as a basis, the following method was evolved:

Apparatus—Before determinations of chloropicrin concentrations can be made physiologically, the eyes of the operators must be calibrated by exposure to know concentrations of gas in air and recording the time of the eye reaction. For this work the following apparatus is required:

1—A device for producing a chloropicrin-air mixture of constant concentration consisting of a source of compressed air, a sulfuric acid drying bottle, an empty bottle as a trap, and a "bubbler" bottle of chloropicrin in a bath of melting ice. (Fig. 1)
2—A glycerol-lubricated, ground-glass syringe for transferring gas.
3—A round glass bulb with a short neck which fits into the eye like an eye cup. This should be fitted with a heavily paraffined rubber stopper containing a short piece of capillary tubing. The bore of the capillary should be a trifle larger than the syringe needle.
4—A stop watch for recording time of eye reaction.

Method—The apparatus having been assembled, a sample ranging from 0.1 to 2 cc. is withdrawn from the bubbler with the syringe and introduced into the bulb through the capillary. The bulb is then shaken a few times to mix the gas, the stopper is quickly removed, and the neck of the bulb is placed over the closed eye of the subject. He then opens his eye normally, at the same time starting the stop watch. Within from 3 to 30 seconds, depending, of course, upon the concentration of gas, the subject will have an overpowering impulse to close his eye. At this point the stop watch is stopped and the time recorded. A series of tests should be run, varying the concentration up to the limit of endurance of the subject. Convenient concentrations to test are 2.5, 5, 7.5, 10, 15, 20, and 25 parts per million. From the data thus obtained a calibration curve can be drawn plotting the concentration in parts per million against the time of the eye reaction in seconds. (Fig. 2) The physiologists may be interested in knowing that the eyes of different subjects varied greatly but both eyes of the same subject reacted similarly as far as could be determined.

Having calibrated the eye of the subject, one can determine the concentration of chloropicrin in any vessel or room by simply recording the time to the eye reaction and reading the concentration by reference to the calibration curve of his eye.

ABSORPTION OF CHLOROPICRIN BY FACE PIECES

In preliminary experiments made at the Lakeside Hospital the observation was made that amounts of chloropicrin and phosgene up to 50 parts per million disappeared within 5 minutes when injected into the face piece of both Akron Tissot and Kops Tissot masks. These tests were made with the subject breathing freely into the outer air through a tube, so that the air within the face piece was not changed. The physiological method described made it possible to follow the rate of disappearance of the chloropicrin with considerable accuracy.

For the purposes of the work Akron Tissot and Kops Tissot masks were fitted with the old-fashioned mouthpiece and nose-clip, so that the air inside the face piece would not be changed during the experiment. In some of the tests wherein the interior of the masks was coated with gas-resistant substances, it was found best to attach the mask to an empty bottle. The dead space in the masks was measured by displacement with water while attached to the subjects or to the empty bottle. The gas was put into the face piece by means of a syringe, as described above. After the gas had been put into the mask, the subject was required to shake his head in order to mix gas and air. When the bottle method was used, the entire apparatus was shaken.

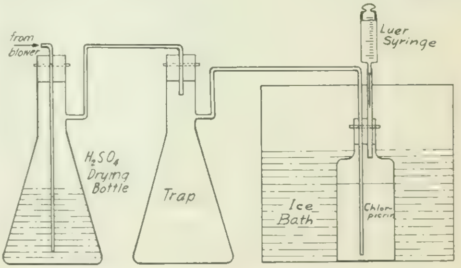

Fig. 1—Apparatus for Obtaining Constant Concentrations of Chloropicrin

When the masks were attached to subjects, the subjects themselves made the determinations at intervals. It was found that a man wearing a mask could make four determinations without removing it. If more than this were attempted, the eyes watered to such an extent that the results were not accurate. When the method of attaching the mask to a bottle was used, the determination was made by applying the eye to the inhalation tube of the mask.

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[1] Received October 19, 1922.

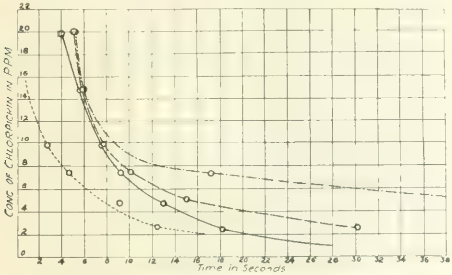


Fig. 2—Calibration Curves of Eyes for Chloropicrin

Tests by the foregoing methods were made on both Akron and Kops masks, both dry and with their interior surfaces wet with water. (Fig. 3) A special test was also made on an Akron mask coated with a 5 per cent gelatin solution, applied uniformly on the interior surface of the mask and allowed to cool to a jelly. The tests were made before the gelatin dried to a film. The result of this test is shown in Table I.

Table I—Absorption of Chloropicrin by Gelatin Coated Akron Tissot Face Piece

Time Minutes	Gas Unabsorbed P. p. m.
At start	30
2	23.5
4	17.0
7	7.5
10	6.5
15	5

Absorption of Chloropicrin by Face-Piece Material

The experiments described showed that gas introduced into the face pieces of gas masks disappeared very rapidly. The fact that wetting the face piece with water and gelatin solution retarded this absorption indicated very strongly that the face-piece material was playing a strong part in absorbing the gas. In order to determine definitely the extent of this absorption, the following experiments were made:

Materials and Apparatus—The face-piece material tested was cut from an Akron Tissot mask. The outer cloth covering of the rubber was stripped off. For each absorption test fresh pieces were cut, measured, and their area calculated.

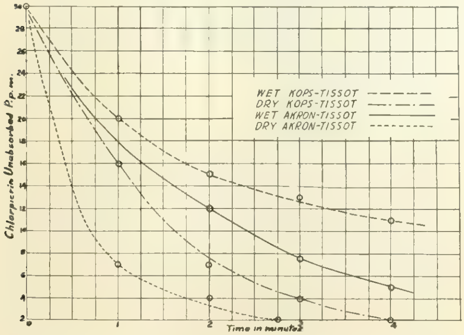


Fig. 3—Chlorpoicrin Absorption Curves of Moist and Dry Kops Tissot and Akron Tissot Masks, with Face Pieces Alone Fitted to Subject

The absorption tests were made in a lamp bulb with its neck shaped like an eye cup, as described above. The bulb was fitted with a heavily paraffined rubber stopper provided with a capillary glass tube through which known quantities of gas were introduced by means of an all-glass syringe. Control tests were made which showed that the paraffined stopper did not absorb a measurable amount of gas during the experiments.

In the first series of experiments comparatively large pieces of rubber were used and the measurements made at intervals of a minute. In the second series small pieces of the material were allowed to come to equilibrium with the gas by standing 18 hours before the final measurements were made. The results are shown graphically in Figs. 4 and 5.

Comparison of Rates of Absorption of Chloropicrin and Phosgene

The results of these experiments left no doubt that small concentrations of chloropicrin are absorbed very quickly when exposed to comparatively large rubber or rubberized surfaces. There were some grounds, however, for doubting the ability of rubber to absorb other gases in equivalent amounts. As phosgene was a very important war gas with markedly different properties, it was decided to compare its rate of absorption by rubber with that of chloropicrin. Of course, the physiological method of analysis could not be used, as phosgene is not a lachrymatory gas. It was necessary, therefore, to resort to chemical methods and to use much heavier concentrations of gas.

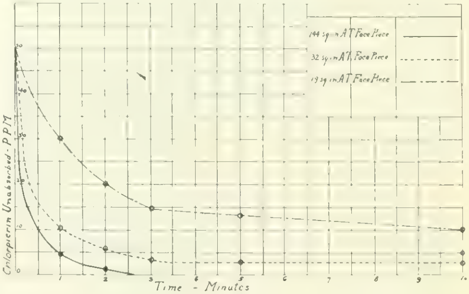


Fig. 4—Curves Showing Rate of Absorption of Chloropicrin by Rubber Face-Piece Material

Materials and Apparatus—The material used for the comparison was cut from an original sheet of face-piece rubber before molding. Strips of this material 1 inch wide and 8 inches long were cut, this being a convenient size for the absorption bulb.

The apparatus consisted of the following:

1—A tubulated glass bulb of 1-liter capacity used as the absorption chamber.

2—A Geissler potash bulb for absorbing and determining the residual gas.

3—A 10-liter aspirator bottle for drawing the gas through the absorbing solution.

Method—The strip of rubber was suspended in the absorption bulb by means of a glass rod and small pieces of wire. A known amount of gas was then put into the bulb by means of a rubber syringe in the case of phosgene, and by a mercury-filled Hempel buret in the case of chloropicrin. The gas was allowed to stand in contact with the rubber for time intervals varying from 15 minutes to 16 hours. At the end of the selected interval the residual gas was drawn through the absorbing solution and analyzed. Control analyses were made on the apparatus to determine the actual amount of gas being put into the bulb. The results are shown in Fig. 6.

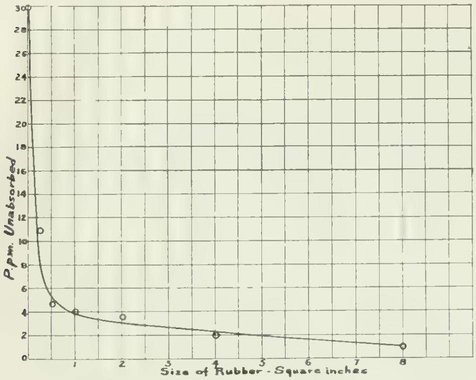


FIG. 5—ABSORPTION OF CHLOROPICRIN BY AKRON TISSOT FACE-PIECE MATERIALS. TIME OF EXPOSURE —18 HOURS

It will be noted that the absorption curves cross at 3 hours' exposure. This indicates that the chloropicrin is absorbed at a faster rate than phosgene, but is also given up at a faster rate when fresh air is drawn into the bulb. When a chloropicrin-containing test piece was dropped into a 500-cc. bottle of fresh air, within 5 minutes the air in the bottle caused the eye to close in less than 4 seconds, indicating that the chloropicrin is given up quite rapidly when the equilibrium is disturbed.

The same is not true, however, of phosgene, and it is probable that there is a chemical combination between the rubber and this gas. With chloropicrin the phenomenon is an apparently simple solution.

DISCUSSION OF RESULTS

A study of this series of experiments cannot fail to lead to the conclusion that rubber and rubberized cloth are very efficient in removing small quantities of war gases from air. It also seems clear that the rate of absorption is rapid enough to account for the fact that men are not gassed in the Tissot type masks even when these masks allow several hundred cubic centimeters of gas-laden air per minute to leak in. In the case of a gas that is not soluble in rubber the protective effect of the face piece would not be in evidence. It happens, however, that the three really important gases—phosgene, chloropicrin, and mustard gas—are all highly soluble. In fact, practically all the gases suggested for war use that are at all suitable for the purpose are sufficiently soluble in rubber to make the protective effect of the face-piece material well worthy of consideration.

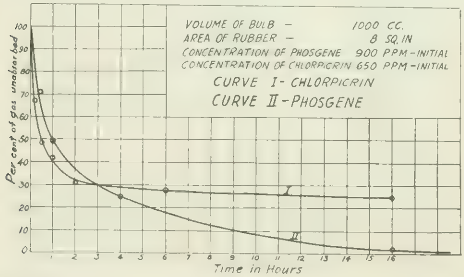


FIG. 6—COMPARISON OF ABSORPTIVE POWER OF RUBBER FOR CHLOROPICRIN AND PHOSGENE

Aside from its relation to war gas problems, the physiological method of gas determination herein described should be of assistance in determining the extent and rate of absorption of many vapors. Data of this kind should be valuable in the study of problems of sanitation, ventilation, hygiene, and occupational diseases.

ACKNOWLEDGMENT

The writer wishes to extend his sincere thanks to R. G. Pierre for his coöperation and suggestions, and to Stanley K. Reimann and Rolland R. Etter for their active assistance.

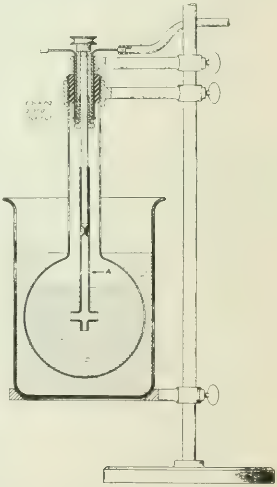
A Gas-Tight Stirrer[1]

By George E. Holm and George R. Greenbank

BUREAU OF ANIMAL INDUSTRY, WASHINGTON, D. C.

THE accompanying cut illustrates the principal features of the stirrer. The bearing and the shaft are machined from steel and hardened, and the shaft is then lapped to fit the bearing with the use of fine emery. The construction of the stuffing box is fully explained in the diagram. The packing used may be cotton waste saturated with the same oil as that used for lubrication. Brass inlet and outlet tubes of $^1/_{16}$-inch diameter are soldered into grooves made in the bearing. Although the apparatus may be constructed in dimensions suitable to the work in which it is to be used, the size found most suitable in laboratory work was of the following dimensions: length of bearing, $2^1/_4$ inches; diameter of bearing, $^5/_8$ inch; length of shaft, 7 inches; diameter of shaft, $^1/_4$ inch; diameter of stuffing box, $^3/_8$ inch.

The glass stirrer is fastened to the shaft with litharge-glycerol cement. It is closed to prevent contact of the liquid with the metal shaft, and contains a small hole, *A*, just above the level of the liquid. Upon rapid stirring, the gas above the liquid is drawn through this hole and the liquid is drawn in through the lower end of the stirrer. Both are thrown out through the arms of the stirrer, thus producing a continuous circulation and mixing of the liquid and the gas in the vessel under a constant gas pressure.



The apparatus shown has been used where thorough mixing of a gas and liquid was desired and where it was desired to measure the quantities of gas absorbed by a liquid in successive intervals of time. The stirrer may be run at a high speed for a long time without great wear, and will also permit relatively high vacuum or pressure within the vessel, without danger of gas leakage.

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[1] Received September 26, 1923.

The Effect of Various Pigments upon the Rate of Oxidation of Linseed Oil[1]

By F. H. Rhodes and A. E. Van Wirt

Cornell University, Ithaca, N. Y.

In the work described in this article an attempt has been made to determine quantitatively the effects of some of the more common white pigments upon the actual rate of oxidation of linseed oil. Films of weighed amounts of paints, prepared from known weights of pigment and linseed oil, were exposed to pure oxygen at constant temperature and pressure, and the rates of absorption of oxygen and of evolution of volatile matter were measured. A number of such experiments were made, using paints prepared from some of the more important and more commonly used white pigments, and the results obtained with the different paints were compared.

IT IS well known that the nature of the pigment present in a paint has a distinct influence upon the rate of drying of the paint and upon the characteristics of the film obtained after drying is complete. For example, the drying is accelerated by white lead and retarded by carbon black, while a paint made from zinc white dries to a harder and more brittle film than does a paint made from white lead. Sabin[2] has shown that the change in weight undergone by a paint film during drying depends upon the nature of the pigment present in the paint; while Gardner[3] points out that the composition of the volatile matter given off during the drying depends upon the pigment used in the paint. Boughton[4] found that the drying of linseed oil is accelerated more by white lead than by zinc white, and more by zinc white than by china clay. Various other investigators have studied this problem of the effect of pigments upon the drying of linseed oil, but the data that have been published upon this subject are more or less fragmentary and sometimes contradictory.

Most of this previous work has been of a qualitative rather than of a quantitative nature. The rates of drying of the paints have been determined by measuring the rates of change in weight of paint films exposed to the air or by noting the times required for the films to become dry to the touch. The change in weight of the film is not an accurate measure of the extent to which the oil has been oxidized, since the oxidation is accompanied by an evolution of volatile matter and the amount and the nature of this volatile matter may vary with the nature of the pigment present in the paint and with the conditions under which the oxidation takes place.[3,5] The time required for the film to become dry to the touch is not a satisfactory criterion of the rate of oxidation of the oil, since, as we shall show, the apparent "dry point" does not always coincide with the same stage in the oxidation. This previous work, therefore, while it may have served to show qualitatively the effect of the nature of the pigment upon the rate of *drying* of the paint, has afforded little quantitative information as to the effect of the pigment upon the progress of the oxidation of the oil.

Apparatus (Fig. 1)

A wide-mouthed suction flask was placed in a thermostat which was kept at 30° C. (±0.2°). The mouth of the flask was closed tightly with a rubber stopper. At the bottom of the stopper was a small hook, from which was suspended a frame of copper wire carrying two strips of cloth, each 2 cm. wide and 10 cm. long. To the side arm of the suction flask was attached a capillary glass tube extending to the top of a mercury-filled Hempel buret. A side arm from this capillary was attached, through a small manometer, with a glass bulb filled with air and immersed in the water within the thermostat. The bottom of the suction flask was covered with a layer of soda lime, and one or more vials of concentrated sulfuric acid were placed within the flask. The soda lime and the sulfuric acid served to absorb the carbon dioxide, water vapor, and volatile organic matter which might be evolved during the drying of the paints and the presence of which might affect the results obtained. The apparatus was placed in a dark corner of the laboratory and the flasks containing the films of paint were, of course, submerged in water, so that practically all light was excluded from the oxidizing films.

Procedure

The buret was filled with pure oxygen, and oxygen was blown through the flask until all the air was displaced. The cloths on the frame were weighed, coated with enough paint to give an even film without running or segregating, and again weighed. Approximately the same amount of paint (1.8 grams, corresponding to about 0.72 gram of oil) was taken in each experiment, and the sample was spread out to a film of the same area in each case. After the sample was weighed the cloths were suspended in the flask, the flask was rinsed out again with the oxygen, and the stopper was forced firmly into position. The amount of oxygen in the system was adjusted until the buret contained exactly 100 cc. of oxygen when connected with the flask and when the entire system was at atmospheric pressure. The reading on the manometer between the comparison bulb and the capillary tube, and the barometric pressure and the temperature of the buret were noted. At intervals, as the oxygen was absorbed, the level of the mercury in the buret was raised until the manometer was restored to its original reading and the volume and the temperature of the unabsorbed oxygen in the buret were observed. From the readings thus taken the weights of oxygen absorbed during the various intervals of time were calculated. After each reading the system was left standing under a pressure slightly greater than atmospheric, while before each read-

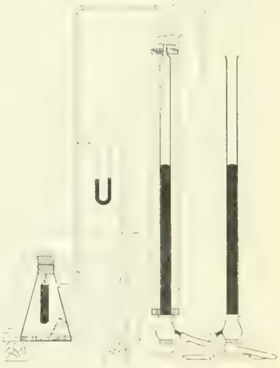

Fig. 1

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[1] Received May 2, 1923.

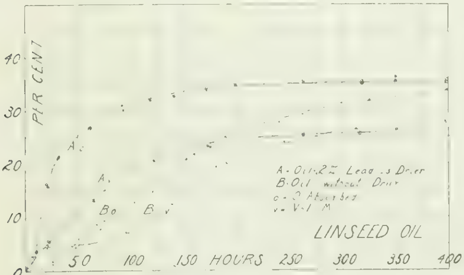
[2] This Journal, **3**, 81 (1911).

[3] *Ibid.*, **6**, 200 (1914).

[4] *Bur. Standards, Tech. Paper* **71** (1916).

[5] Coffey, *J. Chem. Soc.* (*London*), **119**, 1152 (1921).

ing the pressure within the system was slightly less than the initial pressure, so that the average pressure was substantially equal to the initial atmospheric pressure. Since the readings were taken at frequent intervals the variations in pressure were so slight as to be negligible. Several times during each run the sample of paint was removed from the flask and weighed. From the data thus obtained the amount of volatile matter—the difference between the actual weight of the sample and the sum of the original weight of the sample plus the weight of the absorbed oxygen—was determined. Whenever the flask was opened to remove the sample for weighing, the entire system was blown out with oxygen to remove any gaseous impurities that might have escaped absorption by the soda lime or the sulfuric acid. No difference was ever observed between the rates of absorption immediately before and immediately after sweeping out the system in this way, so that any unabsorbed volatile matter, if present, had no appreciable effect upon the rate of absorption of oxygen.



CURVE I.

Materials Used

The linseed oil used in these experiments showed the following analysis:

Specific gravity at 15° C	0.9335
Iodine number (Hanus)	189
Saponification number	196
Acid number	0.83
Refractive index at 15° C	1.4086

To this oil was added an amount of drier solution, prepared from lead linoleate and linseed oil, sufficient to give 0.2 per cent of lead in the finished vehicle. This oil containing the lead drier was used in all the experiments unless otherwise noted.

The pigments used in making up the paints were: silex, barium sulfate (precipitated), Carter process white lead, zinc white (Florence green seal), lithopone (70 per cent barium sulfate, 30 per cent zinc sulfide), basic sulfate of lead, leaded zinc (25 per cent lead sulfate, 75 per cent zinc oxide), titanox pigment—all furnished by a paint manufacture; and barium sulfate (precipitated from barium chloride) prepared in the laboratory.

From each of these pigments a paint was prepared by mixing 33.3 grams of the pigment with 50 grams of the vehicle (oil containing the lead drier) and grinding the mixture thoroughly to secure uniform incorporation. Each paint was allowed to stand in a tightly sealed container for about 3 weeks before use.

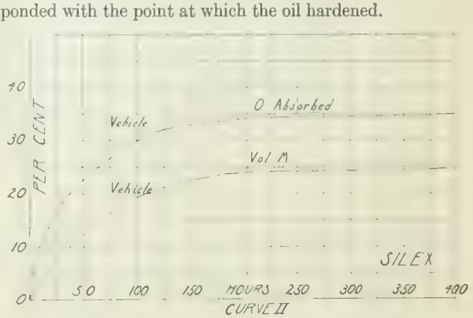
Rate of Oxygen Absorption by Vehicle Alone

The first experiments were made to determine the rate of absorption of oxygen by the vehicle alone. Two such runs were made in order to find out whether or not the method used would give consistent results. The results of these experiments are shown graphically by Curve I-A in which the amounts of oxygen absorbed by the oil and the amounts of volatile products formed during the oxidation (each expressed in terms of percentage by weight of the original oil) are plotted against the lengths of time of exposure. The results obtained in the two experiments were in very close agreement. In each case the oil oxidized rapidly at first, but the rate of oxidation decreased progressively and became very slow indeed after about 300 hours. The actual weight of the oxygen absorbed during the period of observation was about 36 per cent of the original weight of the oil.

It will be observed that at the very beginning of the oxidation there was a "period of induction" during which the absorption of oxygen proceeded relatively slowly. This would seem to indicate that the lead linoleate was not the real catalytic agent in the oxidation of the oil—or, at least, that the lead linoleate was not the only catalytic agent which accelerated the drying. Apparently, there was being formed, during this period of induction, some oxidation product which served to promote the union of the oxygen with the oil. These results support the hypothesis, which has been advanced by a number of investigators, that the oxidation of linseed oil is an autocatalytic reaction.[6]

The formation of volatile matter by the oxidation of the oil proceeded rapidly at first, but more slowly as the rate of oxidation decreased. The total amount of volatile matter formed during the period of observation was about 26 per cent of the original weight of the oil.

For purposes of comparison, a run was made to determine the rate of oxidation of the linseed oil alone, without drier. The oil used was from the same lot as that used in making the vehicle employed in the experiment described above. The results are shown graphically by Curve I-B. The oxidation of the oil alone proceeded much more slowly than did the oxidation of the oil containing the lead drier. The total amount of oxygen absorbed during the period of observation was somewhat less than the amount taken up by the oil containing the lead linoleate, but from the slopes of the curves it appears probable that the oil alone would ultimately absorb as much oxygen as would the oil made up with the drier. The form of the oxidation curve is rather interesting. During the first 15 hours oxidation took place very slowly. After this "period of induction" the oil absorbed oxygen at an almost uniform rate until about 27 per cent of oxygen had been taken up. The fact that the rate was constant throughout this period instead of decreasing as the oxidation proceeded may indicate that the formation of the autocatalyst was not completed during the first period of induction, but continued throughout at least the early part of the period of oxidation. The break in the oxidation curve at the end of the first 200 hours corresponded with the point at which the oil hardened.



CURVE II

Volatile matter was given off rapidly during the first 20 hours' exposure. The high rate of volatilization during this period may have been due, in part at least, to the simple evaporation of certain volatile compounds present in the oil at the beginning of the experiment. Following this first period of rather rapid evaporation, volatile matter was given off slowly at first and then more rapidly until the hardening point of the oil was reached. From this point until the end of the experiment the evolution of volatile matter continued rather slowly. It will be observed that the oil without the drier gave slightly more volatile matter than did the oil to which the drier had been added.

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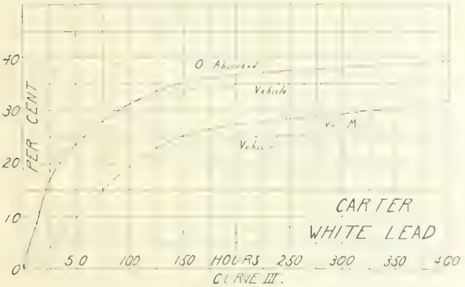
[6] Fahrion, *Chem. Ztg.*, **28**, 1196 (1904); Genthe, *Z. angew. Chem.*, **19**, 2087 (1906); Orloff, *J. Russ. Phys.-Chem. Soc.*, **43**, 1509 (1911).



CURVE III.

SILEX ADDED

The rate of drying of a paint made from silex and the vehicle is shown on Curve II. For purposes of comparison, the curves for the vehicle alone, without pigment, are also shown. In these curves, as in all the curves accompanying this article, the amounts of oxygen absorbed and of volatile matter given off are expressed in terms of percentages by weight of the *oil* in the sample of paint exposed.

It will be observed that the addition of the silex did not materially affect either the rate of absorption of oxygen or the rate of formation of volatile matter. The slight differences which were produced by the presence of the silex may or may not be significant. Apparently, this pigment accelerated the rate of formation of the autocatalyst and thus shortened the period of induction. After about the fifth hour the rate of oxidation began to decrease slightly, owing possibly to the effect of the silex in increasing the thickness of the film and thus increasing the distance through which the oxygen must diffuse to reach the unoxidized oil. After about the fiftieth hour this effect began to disappear. That silex does not permanently decrease the rate of oxidation may be explained by assuming that in the later stages of the oxidation the actual rate of combination of the oil with oxygen, rather than the rate of diffusion, becomes the controlling factor in determining the rate of reaction; or it may be explained by the hypothesis that the silex tends slightly to delay the hardening of the oil and thus keeps the film somewhat more permeable to oxygen during the later stages of the reaction. After about 110 hours the oxidation curve for the silex paint was substantially identical with the oxidation curve for the vehicle alone. These results indicate that silex has little specific effect upon the rate of oxidation of linseed oil.

CARTER WHITE LEAD ADDED

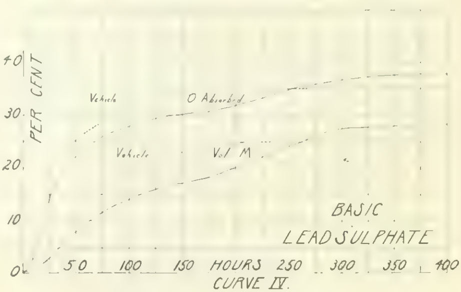
The effect of Carter process white lead is shown by Curve III. In this case, as in the case of the silex, the addition of the pigment increased the thickness of the film and therefore slightly retarded the absorption of oxygen during the earlier stages of drying. Unlike the silex, however, the white lead increased the total amount of oxygen ultimately absorbed by the oil. This drying effect became apparent after about 100 hours' exposure. The total amount of oxygen taken up in 400 hours was about 39 per cent of the weight of the oil, while the vehicle alone absorbed only about 36 per cent; the total amount of volatile matter formed was about 32 per cent, while the vehicle without the pigment evolved only about 26 per cent. It is apparent, therefore, that the Carter process white lead does have some effect in increasing the amount of oxygen absorbed by linseed oil, although this effect is not apparent during the earlier stages of the oxidation.

EFFECT OF BASIC LEAD SULFATE

Curve IV shows the effect of the basic lead sulfate. This pigment gave results somewhat similar to those obtained with Carter process white lead, but the retarding effect in the earlier stages of the drying was more pronounced and continued for a longer time, while the accelerating effect in the later stages of the oxidation was not so great. The differences between the effects of the two pigments may be due to the smaller particle size and the slighter basicity of the basic sulfate. Being finer than the white lead, the sulfate might be expected to interfere more seriously with the diffusion. The sulfate pigment is less strongly basic that the carbonate white lead, and therefore does not react so readily with the oil to form the lead salts, which tend to act as oxygen carriers and to compensate in part for the delay caused by the slower diffusion.

EFFECT OF LITHOPONE

The results obtained with the paint made from lithopone are shown in Curve V. It will be observed that lithopone retards the rate of oxidation and decreases both the amount of oxygen absorbed and the amount of volatile matter given off. The total amount of oxygen absorbed in 400 hours was only 27 per cent of the original weight of the oil; the total amount of volatile matter produced was only 16.4 per cent of the weight of the oil. It is interesting to note that if the effect of the lithopone upon the drying of the oil had been measured simply by determining the change in weight of the film, the results would have led to the very incorrect conclusion that this pigment accelerates the oxidation and does not affect the amount of oxygen ultimately absorbed.



CURVE IV.

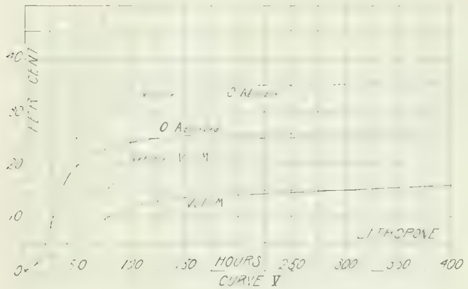
EFFECT OF TITANOX PIGMENT

The effect of the titanox pigment, as shown by Curve VI, was very similar to that of the lithopone. The titanox decreased the rate of absorption of oxygen and of evolution of volatile matter, and decreased the amount of oxygen absorbed and the amount of volatile matter given off.

EFFECT OF LEADED ZINC PIGMENT

The behavior of the paints made from the leaded zinc pigment is shown by Curve VII. With these paints two runs were made. In each case the paint absorbed oxygen more slowly than did the vehicle alone, and the amount of oxygen taken up and the amount of volatile matter given off were much smaller than in the case of the vehicle without pigment.

In the first experiment (Curve VII-A) the absorption of oxygen took place rapidly during the first 55 hours and then stopped. Volatile matter was given off rapidly at first, but slowly after the fifty-fifth hour. The breaks in the two curves occurred simultaneously with the setting of the paint.



In the second experiment (Curve VII-B) the paint began to set in about 40 hours, but the setting and hardening were not complete until about the end of 110 hours. The total amount of oxygen taken up was the same as in the first run. Because of the fact that the film did not harden so quickly but remained permeable for a somewhat longer time, more volatile matter was given off in the second run than in the first.

A certain similarity may be observed in the behavior of the paints made from lithopone, titanox, and leaded zinc. In each case the pigment retards the absorption of oxygen and the evolution of volatile matter and decreases the amount of oxygen ultimately absorbed and the amount of volatile matter ultimately given off. This decrease in the rate and extent of oxidation does not necessarily increase the time required for the paint to become dry, since some of these pigments cause the paint to set and harden at an early stage in the oxidation.

Effect of Barium Sulfate

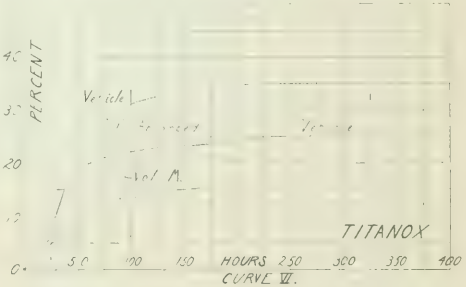
Barium sulfate as a paint pigment gave some very interesting results (Curve VIII). In the first run, made with the barium sulfate furnished by a paint manufacturer, the pigment retarded the oxidation and decreased the amount of oxygen absorbed (Curve VIII-A). These results were contrary to anticipations. Since barium sulfate is theoretically an inert pigment, it was expected that it would give results similar to those obtained with silex—i. e., that it would retard the rate of oxidation but not materially affect the total amount of oxygen ultimately absorbed. Upon examination, it was found that the pigment used contained appreciable quantities of sulfides—presumably, barium or sodium sulfide carried down with the pigment in the original precipitation and not removed by the subsequent washing. The unexpected behavior of the paint made with this pigment may have been due to the presence of this sulfide.

A sample of barium sulfate was prepared in the laboratory by adding an excess of a dilute solution of barium chloride to dilute sulfuric acid and washing and drying the resulting precipitate. This pigment was, of course, free from sulfides, but it did contain a small amount of adsorbed barium chloride. With a paint made from this pigment two runs were made. The results obtained were practically identical, and are shown by Curve VIII-B. The barium sulfate made in the laboratory, like the commercial product, retarded the oxidation in the initial stages of the reaction and decreased the total amount of oxygen taken up, although its effect in cutting down the amount of oxidation was not so pronounced. The amount of volatile matter was very greatly increased and was always greater than the amount of oxygen absorbed, so that the film of paint decreased in weight continuously from the beginning to the end of the period of exposure. The amount of volatile matter given off was more than half the weight of the oil in the original film, and the final film was very thin and dry. The sulfuric acid placed in the reaction chamber to absorb the volatile matter became almost black and had the odor of burnt sugar; whereas in all the other experiments the acid darkened only slightly and remained odorless. Furthermore, the oxidation products from the oil attacked and corroded the copper frame on which the cloths were supported. No evidence of such corrosion was observed in any of the other experiments. Obviously, the barium sulfate in this paint affected not only the rate at which the oxidation proceeded, but also the nature of the oxidation reaction and the character of the products formed thereby.

Effect of Zinc Oxide

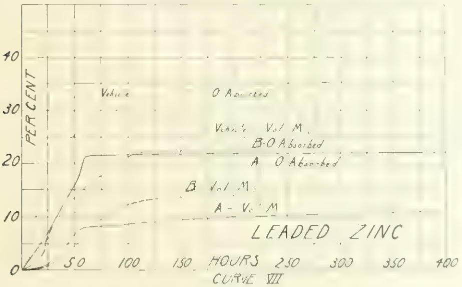
With the zinc oxide paint four runs were made and four distinctly different sets of results were obtained. These results are shown graphically by Curve IX. It will be observed that in each case the initial rate of absorption of oxygen was much lower than the rate of absorption by the vehicle without pigment. This might be expected, since zinc oxide is a very finely divided pigment and should tend greatly to reduce the rate of diffusion of oxygen into the oil. It will also be noted that in each case the total amount of oxygen absorbed during the period of observation was less than the amount absorbed by the free vehicle in similar time, and that the amount of volatile matter given off was less than the amount evolved by the vehicle alone under similar conditions.

In the first experiment (Curve IX-A) the absorption of oxygen took place uniformly and fairly rapidly during the first 120 hours and very much more slowly thereafter. The rate of evolution of volatile matter was very slow at first, but increased rapidly during the first 120 hours. At the end of this time there was a sharp break in the volatile matter curve, and during the latter part of the run volatile matter was given off slowly and at a fairly uniform rate. The form of the curve during the earlier stages of drying suggests that the oxidation of linseed oil may, under certain conditions, proceed in a number of more or less consecutive stages, and that the production of volatile matter is less rapid during the primary stages of the oxidation.



In the second experiment (Curve IX-B) the initial oxidation took place somewhat more rapidly, although not so rapidly as in the case of the vehicle alone. The paint began to harden after about 40 hours' exposure, and was hard at the end of 90 hours. The curve for the evolution of volatile matter showed neither the rapid rise nor the abrupt break that were observed in the first run. In this second experiment the paint began to set before the reaction, which is responsible for the formation of most of the volatile matter, could proceed to any considerable extent.

In the third run (Curve IX-C) the rate of oxidation during the early part of the reaction was identical with that in the second experiment. The setting occurred suddenly, however, after about 40 hours' exposure. It will be noted that the break in the oxidation curve at this point is very abrupt.



CURVE VII

In the fourth experiment (Curve IX-D) the rate of oxidation during the first 40 hours was the same as that in the second and the third runs. Setting took place suddenly at the end of the fortieth hour. Apparently, the film obtained by the setting of this sample was very much less pervious than the hardened film in the third experiment, since very little oxygen was absorbed and very little volatile matter was produced after setting occurred. In this last experiment, the paint made from zinc white gave results very similar to those obtained in the first run with the paint containing leaded zinc.

In the case of the zinc oxide paint, therefore, four samples gave four different types of results. The differences in the results may be explained by the fact that the various samples set and hardened at different rates and at different stages in the oxidation, and gave films of different hardnesses and permeabilities. In the first run setting took place rather gradually, but after about 125 hours the set film underwent a sudden hardening that markedly decreased its permeability; in the second experiment the setting and hardening took place at an earlier stage in the oxidation, but less suddenly; in the third and fourth runs setting and hardening were practically simultaneous and took place suddenly, but the hardened films differed in permeability. There is no apparent reason for the fact that four samples of the same paint, when exposed under as nearly as possible identical conditions, set and hardened at different stages in the oxidation and formed films of different permeabilities.

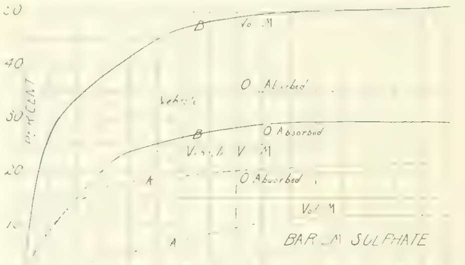
CONCLUSIONS

Evidence has been secured in support of the hypothesis that the drying of linseed oil is an autocatalytic reaction. The real catalyst is an oxidation product of the oil itself. The well-known effect of lead salts in accelerating the drying of the oil is due to the fact that these salts act as pseudo-catalysts to promote the formation of the autocatalysts and thus increase the rate of oxidation when the oil is first exposed to the air. The lead drier does not appear to have any marked effect upon the total amount of oxygen ultimately absorbed by the oil in drying.

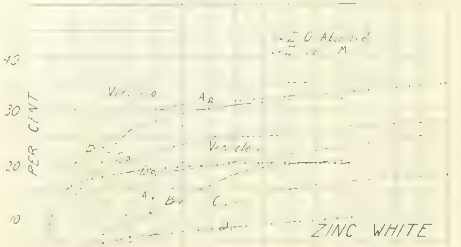
The addition of a pigment to the oil may have a marked effect upon the rate of absorption of oxygen and the rate of evolution of volatile matter, and upon the amount of oxygen absorbed and the amount of volatile matter given off. Upon the basis of their effects upon the oxidation of linseed oil we may distinguish several more or less separate groups of pigments.

The pigments of the first group, of which silex is an example, have little or no effect on the oxidation other than that due to the fact that they increase the thickness of the film and thus decrease the rate of diffusion of oxygen into the oil. Such pigments retard the oxidation, but do not appreciably alter the amount of oxygen ultimately absorbed or the amount of volatile matter ultimately evolved.

The pigments of the second group, which includes such apparently dissimilar substances as leaded zinc, lithopone, titanox, and barium sulfate contaminated with a small amount of sulfides, slow down the oxidation and the evolution of volatile matter and materially decrease the amount of oxygen absorbed and the amount of volatile matter given off. Such pigments appear to owe their effects, in part at least, to the fact that they cause the oil to harden at an earlier stage in the oxidation than does linseed oil without pigment. Such pigments may or may not shorten the apparent drying time. If the pigment greatly decreases the initial rate of oxidation or if it has comparatively little effect in accelerating gelatinization, the drying time may be increased; if the pigment greatly accelerates gelatinization or if it only slightly retards oxidation, it may shorten the time required for the paint to set and dry. It is to be expected that such pigments may affect the character of the paint film—the hardness, brittleness, etc.—not only by their mechanical action as aggregates in the paint concrete, but also by determining the degree of oxidation of the oil in the hardened film, the amount of oil lost by the formation of vapors, and the rapidity with which the solidification of the oil proceeds. Future investigation of the exact effects of various substances on the hardening of linseed oil may afford information which will enable us more closely to control the characteristics of the paint films.



CURVE VIII.



CURVE IX.

The third group of paint pigments includes those which tend to increase the amount of oxygen absorbed by the oil and the amount of volatile matter given off. This group includes such pigments as Carter white lead and basic lead sulfate. These substances generally tend to retard the initial oxidation, the retardation being due, presumably, to the fact that the pigment interferes somewhat with the diffusion of the oxygen into the film. During the latter stages of the oxidation the pigment acts as a drier to increase the amount of oxygen absorbed by the oil. The very fine and only slightly basic sublimed white lead more markedly retarded the initial oxidation and less markedly accelerated the final oxidation than did the coarser and more strongly basic Carter process white lead.

The behavior of zinc white is very interesting. In some cases this pigment acts as an inert pigment like silex—it decreases the initial rate of oxidation but does not materially decrease the amount of oxygen ultimately taken up or the amount of oxygen ultimately evolved. In other cases the zinc oxide behaves like lithopone or leaded zinc in that it causes the oil to harden at an early stage in the oxidation and thus decreases the amount of oxygen absorbed and the amount of vapors given off.

Further work on the study of the effect of pigments on the drying of linseed oil is in progress.

The Vapor Pressures of Some Substances Found in Coal Tar[1]

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Illinois Wesleyan University, Bloomington, Ill.

A simple method for determining vapor pressures of organic compounds has been described.

The vapor pressures of naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, and carbazol have been determined and the results compared with other published data.

The latent heats of vaporization, the sublimation pressures of anthracene and carbazol, and the heats of sublimation have been calculated.

The purposes of this article are (1) to describe a simple yet reliable method for the measurement of vapor pressures of organic compounds, and (2) to present the results of measurements upon some commercially important substances found in coal tar—viz., carbazol, phenanthrene, anthracene, fluorene, acenaphthene, and naphthalene.

Smith and Menzies[2] have reviewed the principles underlying the exact measurement of vapor pressures, and more recently Nelson and Senseman[3] have given a brief but excellent summary of the literature relative to these particular substances. It is manifestly unnecessary to further survey the history of the subject at this time.

The Apparatus and Its Manipulation

The apparatus employed for measuring the vapor pressures is a modification of the static isoteniscope method described by Smith and Menzies.[2] (Fig. 1) It is simple in design and is constructed of such materials as are commonly found around laboratories of moderate means. Only the essential parts of the apparatus need be described.

The construction of the isoteniscope is evident from Fig. 1. The manometer, M, is of the ordinary open-tube type fitted with an accurate wooden scale. It is shielded from the heat of the heating bath. The usual precautions as to purity of the mercury and diameter of the tube must be observed. Very rapid and efficient stirring is accomplished by a small, high-speed, direct-connected motor. The heating bath, A, is a 250-cc. Pyrex beaker containing a suitable liquid. In this work glycerol for the low and the eutectic mixture of the nitrates of sodium and potassium for the higher temperatures are used. Heating is accomplished by a Tirrill burner, the flame of which is easily regulated to produce either rapid or slow changes of temperature. Temperatures of the heating bath are read by means of short-stem boiling-point thermometers graduated to 0.2 degree. These thermometers have the advantage that they can be immersed completely in the bath and the stem correction is thus avoided. A pump, H, is used for reducing the pressures and a 20-liter bottle, G, serves as reservoir. The complete apparatus is set up as a single unit on a small table fitted with two rigid uprights and crossbar as shown in the diagram.

To manipulate the apparatus, the bulb of the isoteniscope is cut off from the U-tube and charged with such an amount of the material to be studied that, when melted, it will about half fill the bulb and the U-tube to some distance below the two smaller bulbs. It is then resealed to the U-tube and clamped into position. The pressure in the closed system is brought to the highest value to be observed by pumping in air through the stopcock, I, or by diminishing the pressure by means of the pump. The temperature of the bath is then raised until the liquid in the isoteniscope boils freely, C_1 being open. After the liquid has boiled for about 1 minute to drive out gases and volatile impurities and furnish sufficient liquid for the U-tube, the temperature is permitted to fall slowly at a rate not to exceed 0.2 degree per minute at the higher temperatures or 0.5 degree at the lower pressures. Eventually, a temperature is reached at which ebullition ceases and the level of the liquid in the arm of the U-tube joining B begins to fall. When the levels in the two arms of the U-tube are equal, C_1 is closed and the temperature of the bath is read. The difference between the levels of the mercury in the manometer is then noted. The algebraic sum of this reading, after correction, and the corrected atmospheric pressure is the vapor pressure at the temperature observed. C_1 is again opened, the temperature raised, and the boiling-out process repeated, followed by a repetition of the readings as just outlined. A sufficient number of checks are thus made to insure the accuracy of the results. For the next measurement the pressure is slowly diminished until the liquid again boils at a somewhat lower temperature, after which the process described above is repeated, checking each reading after a second or third boiling of the liquid.

It has been found advisable to adopt this procedure in place of that more commonly used in which the liquid in the isoteniscope is brought to constant temperature and the external pressure adjusted to equal the vapor pressure of the liquid. The procedure described above is more rapid and for this apparatus, at least, is more accurate.

The use of thermometers instead of thermocouples and the noninsulated, gas-heated bath instead of the more elaborate electrically heated types may be criticized. The writers believe, however, that, judging from the log P against $1/T$ curves (Fig. 2) the data obtained with this apparatus are at least as accurate as those obtained with the more refined type used by Nelson and Senseman.[3]

Purification of Materials

The starting material for each of the substances used in this work consisted of fairly high-grade products. The carbazol and anthracene were each repeatedly recrystallized from chlorobenzene until the melting points were 245.3° and 216.6° C., respectively. In the case of carbazol the nitrogen content indicated a purity of over 99.0 per cent.

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[1] Received May 7, 1923.

[2] *J. Am. Chem. Soc.*, **32**, 1412 (1910).

[3] This Journal, **14**, 58 (1922).

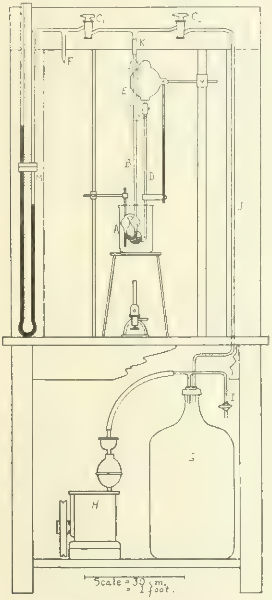

Fig. 1

Two of the most important impurities in phenanthrene are anthracene and carbazol. Pascal[4] has observed that each of these substances forms a series of mixed crystals with phenanthrene, the melting points of which are always higher than that of phenanthrene. It is, therefore, manifestly impossible to purify phenanthrene by recrystallization. Moreover, the vapor pressures of anthracene and phenanthrene differ so slightly that it is not practicable to separate them by distillation. The phenanthrene used in this investigation was purified by first redistilling the sample followed by a partial oxidation with chromic acid and acetic acid. The anthracene is more readily oxidized than phenanthrene. The anthraquinone thus formed was removed first by reducing to anthranol with zinc and caustic soda and then washing the product. The phenanthrene was extracted with benzene and recovered by evaporating to dryness. The product was recrystallized once from alcohol and finally distilled. The middle fraction of this distillate melted at 98.0° C.

The methods employed for the purification of the naphthalene, fluorene, and acenaphthene were similar in that each was repeatedly distilled or sublimed and recrystallized until the melting points were constant, as follows: naphthalene 80.1° C., fluorene 114.2° C., acenaphthene 94.1° C.

TABLE I—NAPHTHALENE

Temperature ° C.	Vapor Pressure Mm.
224.1	881.0
223.9	879.7
223.8	878.5
216.4	737.6
216.45	737.6
202.2	520.0
202.2	519.0
202.1	518.5
189.6	376.2
189.6	376.1
178.0	275.2
177.3	269.7
163.9	181.8
160.9	168.1
149.7	117.9
148.7	114.5
147.8	111.4
132.6	67.0
131.1	63.2
130.25	61.2
127.7	50.1
113.0	32.2
98.1	18.3
87.4	11.9
87.2	11.4

TABLE II—ACENAPHTHENE

Temperature ° C.	Vapor Pressure Mm.
287.8	943.0
287.0	932.3
286.8	930.3
275.4	733.4
275.4	733.4
275.3	733.4
264.4	573.5
264.4	573.1
252.5	434.7
252.4	434.5
247.0	382.9
246.6	377.9
246.2	374.6
233.2	272.0
227.2	234.6
210.4	149.0
210.2	148.0
182.4	63.6
182.4	63.6
147.2	19.2

TABLE III—FLUORENE

Temperature ° C.	Vapor Pressure Mm.
300.4	812.3
299.8	804.3
295.7	738.8
295.7	738.8
295.6	738.8
277.1	490.7
276.6	487.5
241.4	208.4
240.4	205.5
203.0	70.5
202.5	69.5
161.0	18.0

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[4] *Bull. soc. chim.*, **29**, 644 (1921).

DATA OBTAINED

The data obtained are shown in Tables I to VI. These experimental values were then plotted on large-scale coördinate paper (50 x 80 cm.) using the common logarithm of the vapor pressure in millimeters of mercury and the reciprocal of the absolute temperature as the coördinates. This method of plotting furnishes a very useful scheme for judging the accuracy of vapor pressure data. When plotted in this way the points should lie on a very nearly straight line throughout fairly wide ranges of pressure (10 to 1000 mm. at least). This then gives an admirable method for interpolating, or even extrapolating, data to somewhat higher or lower temperatures. Fig. 2 shows graphically a reproduction of some of the data. The values of the vapor pressures at rounded temperatures taken from the log *P vs.* 1/*T* curves are given in Table VII.

TABLE IV—PHENANTHRENE

Temperature ° C.	Vapor Pressure Mm.
346.8	883.9
345.7	870.9
345.1	864.4
337.1	741.0
337.1	741.0
325.4	592.6
324.9	588.7
324.5	584.7
306.5	399.7
306.4	399.2
293.2	299.9
293.2	299.8
293.1	299.7
271.5	183.0
271.5	182.9
246.1	94.6
246.0	94.3
233.8	67.5
203.6	27.2

TABLE V—ANTHRACENE

Temperature ° C.	Vapor Pressure Mm.
340.5	742.2
340.5	742.2
340.6	742.2
328.0	584.0
327.9	583.4
327.4	577.4
313.4	437.0
313.2	436.2
312.8	432.9
300.6	334.2
300.0	331.3
299.9	330.4
282.1	219.8
282.0	219.6
260.3	130.2
259.8	128.3
259.4	127.3
244.6	86.5
244.1	85.9
228.0	55.0
223.2	48.0

TABLE VI—CARBAZOL

Temperature ° C.	Vapor Pressure Mm.
351.8	744.0
351.9	744.0
352.0	744.0
337.5	551.6
336.9	547.4
336.8	543.7
309.0	298.0
308.3	295.8
290.6	193.1
290.0	190.5
289.6	187.9
267.3	105.1
266.6	104.5
266.2	103.6
252.5	70.3
252.6	70.3
252.4	70.0
244.8	55.4
244.8	55.0
	....
...	....

TABLE VII—VAPOR PRESSURES IN MILLIMETERS OF MERCURY, SMOOTHED RESULTS

Temp ° C	Naphthalene	Acenaphthene	Fluorene	Phenanthrene	Anthracene	Carbazol
80	9.6		.	.	.	.
90	13.0				.	
100	19.7				0.045	
110	29.3				0.095	
120	42.9				0.19	
130	61.2				0.38	
140	86.0	14.7			0.73	
150	119.0	21.4	11.9		1.36	
160	162.0	30.5	17.4		2.40	
170	218.5	43.0	24.9	.	4.10	
180	290.0	59.3	34.8	....	6.96	
190	378.5	81.4	48.1	....	11.5	
200	490.0	109.0	65.4	24.6	18.6	7.45
210	630.0	146.0	88.6	33.6	29.2	12.1
220	798.0	192.0	120.4	45.4	43.5	18.9
230	.	250.0	155.0	60.5	58.1	30.0
240	.	323.5	202.0	80.4	77.2	45.1
250	.	410.0	259.5	104.5	100.0	65.5
260	.	520.0	332.0	136.0	129.1	87.3
270	.	650.0	419.0	174.0	165.5	113.5
280	.	808.0	527.0	220.0	210.0	147.0
290	.	998.0	656.0	279.5	265.0	189.0
300	.	..	808.0	347.5	331.0	215.0
310	.	.	....	432.0	409.0	305.5
320	.		...	531.0	501.0	382.5
330	.	..	. ..	648.0	610.0	476.0
340	. .	.		785.0	738.0	586.0
350	. .	. ..	.	946.0	888.0	718.0
Boiling point, ° C.	218.0	277.3	298.0	338.5	342.0	353.0

DISCUSSION OF RESULTS

The results obtained may now be compared with other published data.

Comparing the results shown in the foregoing tables with the corresponding data of Nelson and Senseman,[3] it will be observed that in the case of anthracene there is very close agreement. The experimental data of these investigators for anthracene are not shown in Fig. 2 because of the possibility of confusion with those for phenanthrene. It was observed, however, that both sets of data, when plotted as described above, gave points which were found to lie very nearly on the same straight line.

In the case of phenanthrene and naphthalene the results given here are often very different from those obtained by Nelson and Senseman. Inspection of Fig. 2 indicates that, judging from the standpoint of the log P *vs.* $1/T$ curves, the data of Nelson and Senseman are somewhat in error for these substances. In the case of phenanthrene this may be due to the use of an impure product. The melting point of the phenanthrene used by them was 100.0° C. This, calculated from the melting point curve (unpublished data), is equivalent to at least 5 per cent of anthracene, the presence of which would tend to raise the boiling point and lower the vapor pressure.

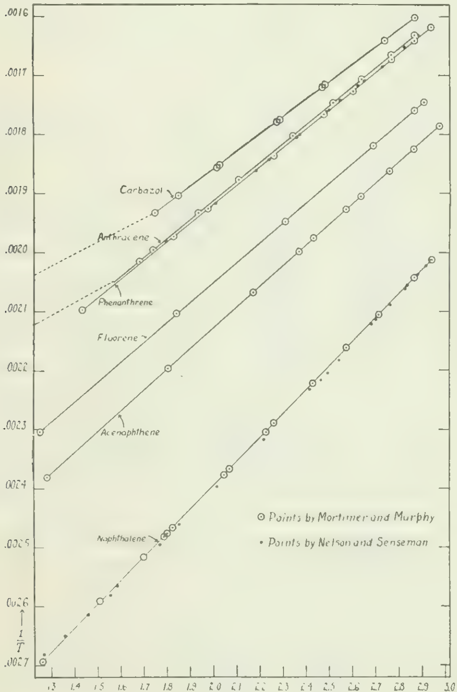

FIG. 2

The presence of impurities, however, will not account for the differences in the case of naphthalene. It is the opinion of the writers that the method used by Nelson and Senseman is at fault, at least for substances which may decompose, in one particular. The heating bath used by them was arranged to give very slow cooling. The writers have found that if cooling takes place too slowly there may be sufficient decomposition of these substances, after the confining liquid stops boiling and before equilibrium is reached, to cause appreciable differences in the measured pressure. At temperatures near the boiling point, equilibrium is reached more quickly and the two sets of data are in fair agreement, the observed boiling points being identical for naphthalene.

Apparently, no measurements of the vapor pressures of acenaphthene, fluorene, and carbazol[5] are given in the literature. The following points have been recorded, and are given here for comparison: carbazol, 338.0[6] and 351.5;[7] fluorene, 305.0[8] and 295.0;[9] acenaphthene, 277.5.[10]

In a recent article Mortimer[11] reviewed the principles relating the vapor pressures and sublimation pressures with the heats of vaporization, sublimation, and fusion. The data given in Table VIII are pertinent to the calculation of the vapor pressures of these substances. This calculation is accomplished by introducing the appropriate values for the constants C and S, found in Table VIII, in the equation, $\log P = C - S/T$, in which P is the pressure in millimeters at the absolute temperature T. The corresponding constants for the calculation of the sublimation pressures of anthracene and carbazol are also included. Similar sublimation pressure data might have been given for the other substances, but on account of the greater extrapolation (lower melting point) the calculation of sublimation pressures for these substances is less accurate.

TABLE VIII

SUBSTANCE	Absolute Boiling Point	S	C	Calories per Mol
Naphthalene	491.0	2465	7.901	10,450
Acenaphthene	550.3	2835	8.033	12,010
Fluorene	571.0	2957	8.059	12,510
Phenanthrene	611.5	2990	7.771	12,660
Anthracene	615.0	3093	7.910	13,100
Carbazol	626	3380	8.280	14,310
Anthracene (solid)	....	4595	10.972	19,990
Carbazol (solid)	....	4780	10.982	20,710

Column 5, Table VIII, contains the values of the molecular latent heats of vaporization (or of sublimation). The values for the heats of vaporization have been calculated from the expression $L = 4.23 \times S$. The constant 4.23 has been used instead of 4.58 (1.9885×2.303), because it has been shown[11] that the constant 4.58 gives results which are about 8 per cent greater than those determined calorimetrically. The heats of sublimation for anthracene and carbazol were calculated by adding the molecular latent heats of vaporization and of fusion.

Finally, a comparison of the calculated sublimation pressures of anthracene may be made with the experimental results given by Niederschulte.[12] It was found that the experimental points given by this observer fell quite closely to the calculated log P *vs.* $1/T$ curve, the deviations being both positive and negative. These calculated sublimation pressures are included in Table VII.

Stelzner[13] has also determined the pressures of anthracene at temperatures below the melting point. Access was not had to the original article, but it is quite evident that the determinations were made on a solution of anthracene rather than on the solid, because the data fall upon the extrapolated vapor pressure curve rather than upon the sublimation pressure curve.

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[5] Since this paper was written Senseman and Nelson, THIS JOURNAL, **15**, 382 (1923), have published data on this substance. The boiling point is found by the authors to be 353° C.; Senseman and Nelson obtained 354.76° C.

[6] Graebe and Glaser, *Ber.*, **5**, 12 (1872).

[7] Chemical Rubber Handbook, **1920**, p. 161.

[8] Barbier, *Ann. chim. phys.* [5], **7**, 479 (1876).

[9] Chemical Rubber Handbook, **1920**, p. 185.

[10] Behr and van Dorp, *Ann. Chem. Pharm.*, **172**, 263 (1874).

[11] *J. Am. Chem. Soc.*, **44**, 1429 (1922).

[12] Landolt and Börnstein, Tabellen, **1912**, p. 394; Dissertation, Erlangen, **1903**.

[13] Landolt and Börnstein, Tabellen, **1912**, p. 394; Dissertation, Erlangen, **1901**.

Dr. Sosman Honored

R. B. Sosman, of the Geophysical Laboratory, has been appointed by the National Research Council as American Member on the Permanent Committee for the Standardization of Physico-Chemical Symbols of the International Union of Pure and Applied Chemistry. The other members of the committee are: Ernst Cohen, University of Utrecht, chairman; Alexander Findlay, University of Aberdeen; and Charles Marie, Sorbonne.

An Improved Method for the Separation of Gas Mixtures[1]

By Fractional Distillation at Low Temperatures and Pressures

By Martin Shepherd and Frank Porter

Bureau of Mines, Washington, D. C.

This paper describes an improved method for the separation of gas mixtures by fractional distillation at low temperatures and pressures. The work was mainly carried out at the Chemical Laboratory, U. S. Helium Plant No. 3, Petrolia, Texas (1920–21).

The method, with suitable modifications, is applicable to many problems of gas separation, and may be employed in a great number of cases where ordinary chemical methods do not give results of sufficient accuracy or cannot be used at all. It may be used in technical work, giving results commensurate with the requirements of engineering calculations. With no modifications other than an increase in the number of fractionations resorted to, it may be employed in precision work, either for the preparation of gases of high purity suitable for the measurement of physical constants, or to effect the exact analytical separation of complex mixtures.

The method is capable of yielding results of greater accuracy than those obtained by previous distillation methods, and attains this end in a small fraction of the time formerly required.

In developing the subject, the general principles of the separation of gases by liquefaction and subsequent distillation are first given; then an account of previous applications, followed by the expression of the need of an improved method, and its development in detail. Illustration is made of the separation of a complex gas mixture containing helium, nitrogen, and the saturated hydrocarbon vapors, and the accuracy of the method set forth. Finally, its application to the preparation of pure gases is described, and the tests of purity of the gases are given.

The separation of gases by distillation differs in several respects from the more common type of distillations of substances boiling above room temperatures. The gas mixtures must first be liquefied. The successive distillations are then made, choosing temperatures at which the more volatile component present in each case possesses a relatively high vapor pressure, and the less volatile components negligible vapor pressures. Since these distillation temperatures are maintained fairly constant for the removal of each component, the fractionation is effected by varying the *pressure* rather than the temperature. Very low pressures are employed, which involve corresponding low temperatures. Two decided advantages accrue from these conditions. The first, and by far the most important, is that the ratio of the vapor pressure of the more volatile component to that of the less volatile components becomes very much greater at the lower temperatures, and so the separation is distinctly sharper. The second lies in the fact that the actual amount of the vapor phase over the liquid phase is quite small at the low pressures, and consequently a negligible amount of the vapor phase remains above the liquid at the completion of each distillation—an important consideration where small amounts of gas are used.

Previous Applications of Fractional Distillation

Ramsay,[2] in his memorable work on the rare gases of the atmosphere, used fractional distillation in the separation of the gas mixtures, and was able not only to obtain the gases in a high state of purity, but also to make very accurate analytical separations.

Adaptations of this method have been used by numerous investigators in the preparation of pure gases and the separation of gas mixtures.[3]

Burrell, Seibert, and Robertson[4] were able, by a method similar to that used by Ramsay, to separate analytically the constituents of natural gas.

A brief description of the apparatus and method used by Burrell, Seibert, and Robertson, will illustrate in a general way those formerly employed. The gas mixture to be analyzed was measured in a buret, transferred to a liquefying bulb surrounded by a cold bath, and a distillate pumped off and collected over mercury. This distillate was then transferred to a buret for measurement. The residue remaining was allowed to warm up and likewise pumped off and measured. Several distillations and combinations of the resulting fractions were necessary to obtain each of the components of the mixture in sufficient purity for accurate results, so that a determination of all the constituents was a long and complicated procedure.

Need of an Improved Method

Gas distillation presented a wide field for extension in 1918, when the Bureau of Mines undertook the production of helium for the Army and Navy Aircraft Divisions.

At the experimental plant erected at Petrolia, Texas, and operating under the Jefferies-Norton system, the chemical laboratory was confronted with the necessity of preparing pure methane, ethane, and propane for vapor pressure measurements; and also with the problem of a systematic investigation of several types of gases peculiar to the liquefaction plant and containing appreciable percentages of the hydrocarbons of the series $C_n H_{2n+2}$, heavier than ethane.

The work was undertaken with the apparatus and method suggested by Burrell, Seibert, and Robertson.[4] It was found that an accurate separation of many of the particular mixtures examined required almost a week's time—i. e., 36 to 48 hours continuous operation. As a plant control method this distillation process was entirely out of the question. It held little value from the more deliberate standpoint of investigation and interpretation of plant operation, since affairs progressed so rapidly that week-old information possessed relatively small importance.

Development of an Improved Method

An apparatus and method was therefore developed which was capable of accomplishing the same results as the previous method, but in a fraction of the time formerly required.

The apparatus constructed employs several improvements in the technic of gas manipulation, which have been in gen-

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[1] Received July 29, 1922. Published by permission of the Director, U. S. Bureau of Mines.

[2] Travers, "Experimental Study of Gases," **1901**, p. 212; Ramsay and Travers, *Proc. Roy. Soc.* (*London*), **63**, 438; **64**, 183; *Phil. Trans.*, **197**, 47 (1901).

[3] Ab-der-Halden, *J. Gas Lighting*, **126**, 342 (1914); Anderson, This Journal, **9**, 142 (1917); Anon., *C. A.*, **11**, 296 (1917); Anon., *Gas World*, **59**, 152 (1913); Bordan and Taplav, *Compt. rend.*, **146**, 628; **147**, 591 (1908); Burrell and Robertson, This Journal, **7**, 209 (1917); *Proc. Am. Gas Inst.*, **9**, 219 (1914); Burrell, Seibert, and Robertson, *Bur. Mines, Tech. Paper* **142** (1916); *Ibid.*, **104** (1915); Czoko, *J. Gasbel.*, **56**, 1172 (1913); Erdmann and Stoltzenberg, *Ber.*, **43**, 1702 (1910); Lebeau and Damiens, *Compt. rend.*, **156**, 144, 325, 797 (1913); *J. Soc. Chem. Ind.*, **32**, 126 (1913); *J. Gas Lighting*, **125**, 105 (1913); Stoltzenberg, *Ber.*, **43**, 1708 (1910); Travers, "Study of Gases," p. 210; Whiton, This Journal, **8**, 733 (1918).

[4] *Bur. Mines, Tech. Paper* **104** (1915).

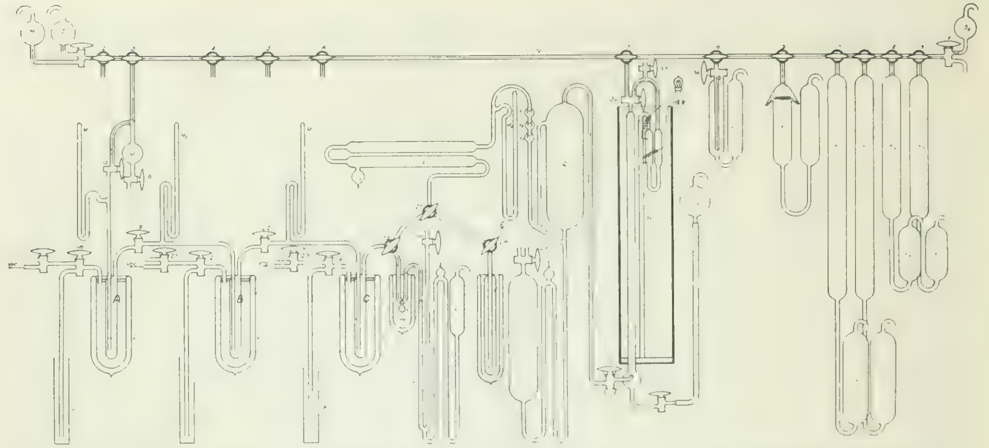

FIG. 1—APPARATUS FOR SEPARATION OF GAS MIXTURES BY FRACTIONAL DISTILLATION AT LOW TEMPERATURES AND PRESSURES

A, B, C = Distillation Bulbs
D_1–D_4 = Dewar Tubes
H = Reservoir for Cleaning Solution
J = Adsorption Pipet
K = Combustion Pipet
L_1–L_7 = Leveling Bulbs
M_1–M_4 = Barometric Manometers
O_1, O_2 = P_2O_5 Tubes
P_1–P_3 = Mercury Seal Pressure Regulators
Q = Töpler Pump
R_1–R_4 = Gas Reservoirs
S_1, S_2 = Mercury Reservoirs
T_1–T_3 = Air Traps
U_1, U_2 = Mercury Traps
V_1–V_3 = Valves for Töpler Pump
W = Gas Measuring Buret
X = Liquefying Bulb for Vapor Pressure Manometer
Z = Vapor Pressure Manometer
(Cap.) Tee Cocks = 2–13
Y Cocks = 25–28
3-Way Cocks = 1, 14, 17, 18, 20, 21, 23, 24, 29, 32, 34
2-Way Cocks = 15, 16, 19, 22, 26, 30, 31, 33
Y = Bulb Filled with Activated Coconut Charcoal
N = Distributor Chain

eral use for some time and were suitable for adaption to this problem. It abandons the older ideas of separate pieces of apparatus, combining, as it does all the necessary steps of gas condensation, distillation, pumping, storage, volume measurement, and distribution into one complete unit, independent of auxiliary parts. The distribution of gas in a mercury-filled train eliminates all dead capillary space.[5] The system of multiple distillation bulbs permits the removal of vapors by rapid condensations, and eliminates the greater part of the work formerly assigned to the Töpler pump.

The details of the apparatus (Fig. 1) and the manner in which a separation is carried out are best described by taking as an example the fractionation of the natural gas from the Petrolia field. This gas has for its constituents helium, nitrogen, methane, ethane, propane, butane, and also small amounts of the higher saturated hydrocarbons. No attempt was made to separate the helium, nitrogen, and methane (this group being treated as a single fraction), since satisfactory temperatures for these distillations were not available, and other methods of analysis of this fraction were preferable from a practical standpoint.

To prepare the apparatus for an analysis, clean mercury is allowed to displace all gas from the distributor train N, Töpler pump head Q, buret W, and reservoirs R. An oil-immersed gear pump connected at Cock 28 quickly evacuates the distillation train, including the trap U, distillation bulbs A, B, and C, the manometer Z, with liquefying bulb X, and the P_2O_5 tubes o, to a pressure of about 0.1 mm. Cock 28 is then turned to a tube Y, filled with activated coconut charcoal and surrounded with liquid air. Complete exhaustion of the distillation train is attained within 3 minutes, by adsorption of the residual air by the cold charcoal. The charcoal tube is then shut off from the train.

The three distillation bulbs are then cut off from one another by the interposing cocks, and surrounded with liquid air contained in closed Dewar tubes. A system of three-way cocks connects the Dewar tubes to the oil-immersed gear vacuum pump, the atmosphere, or a mercury pressure seal, P. By this arrangement the liquid air within the Dewar tubes may be made to boil at pressures ranging from less than 0.1 to 2 atmospheres, and a corresponding temperature range (depending of course on the age of the liquid air) of −180° to −208° C. is available.

The gas mixture to be examined is measured in the buret and then transferred through the distributor train into bulb A, where it partially liquefies at −190° C. It is evident that the nitrogen and helium will not condense at this temperature and a pressure of less than atmospheric, and these two constituents, therefore, never properly enter the actual process of distillation, except to the small degree, due to their slight solubilities as uncondensed gases in the hydrocarbon liquid phase. Their separation may be regarded almost entirely as an actual separation by fractional condensation, a case that will occur very rarely. (It is unfortunate that a great many experimenters have used purely condensation processes under the name of distillation, when an accurate separation could only have been attained by an actual distillation.) It has been found in practice that all the helium and nitrogen, together with a small part of the methane, may be drawn off at once from A, at −190° C., through B and C into the Töpler pump, which delivers directly into the buret for measurement. This fraction carries no ethane with it. A great saving in the time required for any one analysis is effected by this preliminary removal of uncondensed gases. The greater part of the methane now remains with the heavier hydrocarbon fraction in A. In order to accelerate its separation, the liquid air surrounding A is put under pressure, and a temperature of −180° to −183° C. is employed for the next distillation. This raises the vapor pressure of the methane from approximately 4 cm. to between 6 and 10 cm., at the same time keeping the vapor pressure of the ethane well under 0.1 mm. The methane is then transferred from *A* to *B* by simply causing the liquid air in *B* to boil under reduced pressure (at a temperature of, say, −205° C.), which effectively removes methane vapor from *A* and condenses it in *B*. A second distillation from *B* to *C* is made by allowing *B* to warm up to the boiling point of liquid air at atmospheric pressure (−190° C.) and surrounding *C* with liquid air boiling under reduced pressure. Then by closing the cock between *C* and *B* and allowing *C* to warm up to room temperature, the pure methane fraction in *C* is vaporized and easily removed by the Töpler pump to the buret, where it is measured with the uncondensed He + N_2 fraction. The residue of higher hydrocarbons, remaining in *A* and *B*, is now allowed to warm up to room temperature, completely vaporized, and is then recondensed at −183° C. and fractionated as before, in order to free the residue from any traces of methane. This distillate is added to the He + N_2 + CH_4 fraction already obtained. The vapor pressure of ethane always remains so low at these liquid air temperatures that practically none of it is removed with the last methane distillates. In practice, it was found unnecessary to provide for the possibility of ethane being present in the methane fraction, when ordinary analytical separation was desired.

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[5] Allen and Lyder, "Chemical Survey of Natural Gases of Kansas and Oklahoma," p. 39.

The separation of ethane from the remaining higher hydrocarbons is effected in a similar way, except that the distillation temperature employed is between −145° and −150° C., and the receiving temperature is that of liquid air. The vapor pressure ratio of ethane to propane at −150° C. is approximately 4 to 0.4 mm. For the separation of propane from the butane plus heavier hydrocarbon fraction a temperature of −120° C. was used, with a corresponding propane-butane vapor pressure ratio of 5 to 0.2 mm. The various steps for a complete fractionation of a sample of Petrolia gas are shown in Table I. The fractionating diagram here shown differs somewhat from the scheme described in the text, in that it provides for fractionation of possible traces of ethane from the He-N_2-CH_4 fraction.

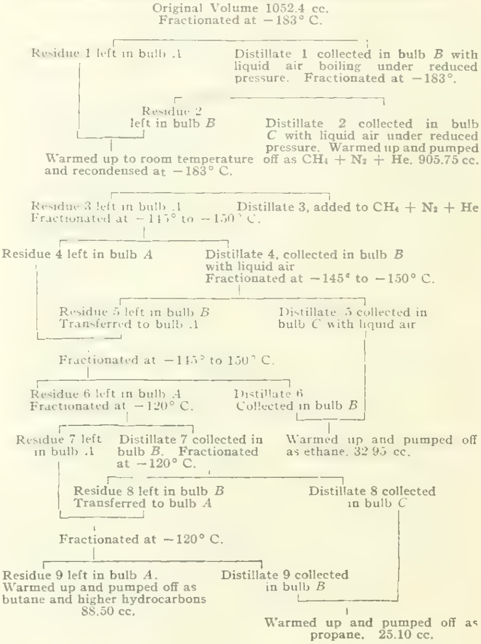
The fractions after measurement may be stored in reservoirs, *R*. The amount of methane in the methane-nitrogen fraction can be determined by combustion, using the combustion pipet *K*[6] and absorption pipet *J*,[7] which preferably are placed on opposite sides of the buret. If percentage helium is desired, it may be determined by the Cady[8] method.

Accuracy of the Analysis

In practice, by following the fractionation chart of Table I, check analyses have agreed within the range 0.02 to 0.10 per cent. It is necessary to employ careful manipulation in order to obtain checks to the second decimal place. It also follows that precision volume measurements, an all-glass apparatus with no rubber connections, accurately ground, and suitably lubricated stopcocks are all necessary requirements. The portions of the apparatus confining gas over mercury must present no gas traps; and at all points where mercury enters the apparatus from air contact, air traps must be provided. An example of such an analysis is given in Table I.

A better test of the accuracy of analyses by fractional distillation of natural gas, according to the method charted in Table I, has recently been made by Frank Porter and F. W. Schroeder in the Cryogenic Research Laboratory, Washington, D. C. Pure methane, ethane, and propane were prepared and tested as follows: Commercial nitrogen was freed from any impurities that would interfere by passing through a bulb surrounded with liquid air. A known mixture of these gases was made up similar in composition to the natural gas from the Petrolia field. This mixture was analyzed, using the regular procedure illustrated in Table I. For the sake of comparison, analysis of the same mixture was made by ordinary combustion with oxygen over a glowing platinum helix, the hydrocarbon fraction being calculated as methane and ethane from the contraction and carbon dioxide, and nitrogen taken by difference from 100. These results as summarized in Table II.

TABLE I—FRACTIONATION OF PETROLIA GAS BY IMPROVED SYSTEM


Original Volume 1052.4 cc.
Fractionated at −183° C.
Residue 1 left in bulb A
Distillate 1 collected in bulb B with liquid air boiling under reduced pressure. Fractionated at −183°.
Residue 2 left in bulb B
Distillate 2 collected in bulb C with liquid air under reduced pressure. Warmed up and pumped off as CH4 + N2 + He. 905.75 cc.
Warmed up to room temperature and recondensed at −183° C.
Residue 3 left in bulb A Fractionated at −145° to −150° C.
Distillate 3, added to CH4 + N2 + He
Residue 4 left in bulb A
Distillate 4, collected in bulb B with liquid air Fractionated at −145° to −150° C.
Residue 5 left in bulb B Transferred to bulb A
Distillate 5 collected in bulb C with liquid air
Fractionated at −145° to 150° C.
Residue 6 left in bulb A Fractionated at −120° C.
Distillate 6 Collected in bulb B
Residue 7 left in bulb A
Distillate 7 collected in bulb B. Fractionated at −120° C.
Warmed up and pumped off as ethane. 32.95 cc.
Residue 8 left in bulb B Transferred to bulb A
Distillate 8 collected in bulb C
Fractionated at −120° C.
Residue 9 left in bulb A. Warmed up and pumped off as butane and higher hydrocarbons 88.50 cc.
Distillate 9 collected in bulb B
Warmed up and pumped off as propane. 25.10 cc.

GAS	VOLUME Cc.	VOLUME Per cent
Original volume of mixture	1052.4	100.00
CH_4N_2He	905.7	86.06
C_2H_6	32.95	3.13
C_3H_8	25.10	2.39
C_4H_{10} + heavier C_nH_{2n+2}	88.50	8.41
TOTAL	1052.2	99.99
Deviation from original volume	0.2	0.01

It will be seen that, with no more than three distillations for each component, the errors are of the approximate magnitude of 0.1 per cent. This error is about equal to the probable error in estimating volumes in the present instance. It is then clearly indicated that the accuracy easily falls within the limits required by all technical gas investigations. It is evident that the accuracy of the method is at the option of the operator. By increasing the number of fractionations for each component, the accuracy can be made to approach the limit imposed by even the most exact method available for measuring gas volumes.

The results of the analysis by the combustion method, however, deviate by approximately 5 per cent from the true values. This deviations should possibly not be considered entirely in the light of a true error, since the greater percentage

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[6] Weaver and Ledig, THIS JOURNAL, **12**, 368 (1920).

[7] *Bur. Mines, Bull.* **42**, gives details of combustion analyses.

[8] Cady and McFarland, *J. Am. Chem. Soc.*, **29**, 1524 (1907).

TABLE II —ANALYSIS OF A KNOWN MIXTURE[a] OF PURE GASES BY FRACTIONAL DISTILLATION

COMPOSITION OF MIXTURE OF PURE GASES				ANALYSIS OF MIXTURE BY DISTILLATION—PER CENT		ANALYSIS OF MIXTURE BY COMBUSTION WITH OXYGEN OVER GLOWING PLATINUM HELIX					
						Composition—Per cent				Per cent Deviation[b] from True Value	
Gas	Cc.	Volume		Composition	Deviation from True Value	(1)	(2)	Average			
Nitrogen	136.80	28.67	88.87	88.99	+0.12	29.7	29.9	29.8	85.3	−3.7	+1.13
Methane	287.25	60.20				55.4	55.6	55.5			−4.7
Ethane	27.85	5.84	11.13	5.85	+0.01	14.9	14.5	14.7	14.7	+3.6	+8.86
Propane	25.25	5.29		5.16	−0.13						−5.29
TOTAL	477.15	100.00	100.00	100.00	0.00	100.0	100.0	100.0	100.0		0.00

[a] Mixture approximates the composition of Petrolia natural gas.

[b] The composition was calculated as if methane and ethane were the only hydrocarbons present, and deviation from true value must necessarily follow.

of the difference necessarily follows from the computation on the basis of the presence of methane and ethane only, which was known to be untrue in the present case. While it is generally known to those familiar with the method that a combustion of a mixture of more than two hydrocarbons affords data insufficient to compute the true percentage composition of the mixture (and this necessarily applies to practically any natural gas), it is thought that a direct comparison like the one offered in the table may bring this fact more forcibly to the attention of engineers, since such deviations from the true composition may introduce serious discrepancies in calculations relating to a gas investigation project concerned with a mixture of this type—as, for example, cryogenic engineering problems dealing with distillations, absorptions, etc., including particularly the gasoline extraction industry. Fortunately, thermal values calculated from such a combustion analysis will be extremely close to the true figures.

It is perhaps worthy of further note that one would expect the figure for total carbon, or residual nitrogen, to be the same whether obtained by combustion or by distillation. The fact that the nitrogen content of the mixture, as indicated by combustion, deviated by +1.13 per cent from the true value, discloses an apparent error inherent in the combustion method, applied to this particular type of gas mixture—or what might be called a "wet" natural gas. Some excuse for this belief lies in the fact that the combustions were carried out in a carefully constructed apparatus, employing a mercury-filled distributor train. The combustion pipet and absorption pipets were placed on opposite sides of the gas-measuring buret, instead of as shown in Fig. 1, and the train, combustion pipet, and buret subjected to a thorough washing with 0.5 per cent acidulated water to remove possible traces of potassium hydroxide after each separate analysis, thereby insuring no absorption of carbon dioxide in the apparatus after the combustion and before the measurement of the contraction. The combustions were conducted with a measured excess of pure oxygen, and the wire temperature was carried as high as possible in order to effect as complete a combustion of methane and the heavier hydrocarbons as possible. After one to two hundred such combustions the black deposit collected from the dome of the combustion pipet revealed the distinct presence of carbon. It would seem doubtful if complete combustion is ordinarily attained over a glowing platinum helix with a "wet" natural gas. This point should, of course, be made the subject of further study.

PREPARATION OF PURE GASES

The preparation of very pure gases, suitable for the measurement of physical constants, is a difficult matter, since in the generation of any gas there is invariably introduced a number of impurities, which in many cases cannot be removed by chemical methods. Especially is this true in the case of organic compounds where the impurities are apt to be homologs of the gas prepared. Fractional distillation is often the logical procedure for final purification.

The procedure for obtaining gases in the pure state is the same as already described, except that the distillations are continued as many times as necessary by transferring the residue left in *B* to *A*, and distillate left in *C* to *B*, and then redistilling from *B* to *C*, discarding the end fractions. A transfer from one bulb to another is made by allowing the one to come to room temperature, while open to the other surrounded with liquid air.

TEST OF PURITY

Vapor pressure measurements have been used as the test of purity, based on the fact that vapor pressure of a pure substance does not change as the ratio of the liquid volume to the gas volume is varied. This seems to be the best available method, and has been regularly employed by Travers, Onnes, and others.[9] The manometer Travers describes was made an integral part of the apparatus, connecting through a three-way cock (*Z*, Fig. 1) to bulb *C*.

In the manner described above, with the prescribed tests of purity accepted as a criterion, pure methane, ethane, and propane were prepared from Petrolia gas. The preparation was repeated in the case of methane, purification being made of a gas generated from methyl iodide in the presence of zinc-copper couple, and passed in succession through palladium asbestos at 100° C., and a condensation tube at −150° C., 760 mm. pressure, before submitting to distillation. The vapor pressure test in no case showed a variation of as much as one millimeter. Spectroscopic examination was used to supplement the vapor test and no nitrogen was detected by this means. The preparation of methane from natural gas by fractionation required about eight hours. The older methods demanded weeks of tedious manipulation to attain the same end.

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[9] Travers, "Study of Gases," p. 228.

European Mining Industry

Remarkable progress has been achieved in the reconstruction of the French mining industry, according to George S. Rice, chief mining engineer of the Bureau of Mines, who has returned to this country after completing a study, occupying several months, of conditions in the mining industries of France, Great Britain, Belgium, Poland, and Czechoslovakia. Underground, the French mines have recovered to such an extent that they are producing about 70 per cent of the normal coal output. When all the water has been pumped out of the mines, the coal production of Northern France will be greatly increased over that of the pre-war period.

Novel methods for obtaining petroleum, involving the mining of oil sands and their subsequent treatment at the surface, are employed in Alsace and near Hanover. This makes possible a greater recovery of the petroleum, two-thirds of which is left in the ground after ordinary extraction by wells.

In Great Britain and France the employment of rock dust as a screen or barrier for the limitation of coal dust explosions to the immediate area of the explosion has been made compulsory. In France powdered coal has been widely adopted as a fuel. In Germany, near Hanover, novel methods are employed in the distillation of brown coal, a lignite quite different from American lignites, from which various oils, paraffin, and gas are being obtained. At Whitehaven, England, coal is being mined under the sea at a point four and one-half miles from the shore line.

As a result of Mr. Rice's visit to England the British government has already proposed that a joint program of research, covering various mining problems, be adopted. This program would include the exchange of technical information, of materials under test, of scientific apparatus, and possibly of research personnel. This proposal has been accepted by Secretary Work.

Indene and Styrene—Constituents of Carbureted Water-Gas Tar[1]

By Ralph L. Brown and Roscoe D. Howard

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THE list of constituents which have been identified and may normally be expected to be present in coal tar is a long one. The compounds comprising this list have been discussed in the authoritative work of Lunge,[2] in which the literature had been well reviewed. In the case of carbureted water-gas tar but little work has apparently been done towards the identification of constituents. In a recent publication, Bateman,[3] in speaking of water-gas tar, states that "benzol, toluol, xylol, naphthalene, phenanthrene, and methyl anthracene have been identified." Downs and Dean[4] reported the identification of thiophene, benzene, toluene, *o*-, *m*-, and *p*-xylenes, mesitylene, naphthalene, and anthracene. In 1893, Deunstedt and Ahrens[5] reported an examination of condensate from the illuminating gas of the City of Hamburg, in which they found about 1 per cent of styrene and an unstated quantity of indene, but from their original paper the amount is judged to be only a few per cent. In a previous paper[6] it was pointed out that the natural condensate, "drip-oil," taken from the distributing systems of carbureted water-gas plants in the United States contained these two hydrocarbons—namely, indene and styrene—in amounts totaling 40 to 50 per cent of the condensate. It follows as a corollary that these two hydrocarbons should be found in water-gas tar. It is the belief of the writers that the most intelligent and profitable utilization of this by-product of the "gross" industry of gas manufacture is possible when it is based upon the fundamental information of molecular composition of the tar, and the physical and chemical properties of the constituents. With this point of view, and in the interests of the dissemination of knowledge, the writers have isolated, identified, and measured the indene and styrene in two typical samples of water-gas tar. The experimental data in their essentials are given below.

DETERMINATION OF STYRENE AND INDENE

	PERCENTAGE OF TAR SAMPLE						MELTING POINTS—° C.					
		Fractions					Styrene Dibromide			Indene Oxybromide		
Sample	Oils Boiling below 190° C.	1	2	3	Styrene	Indene	From Fraction 2	Pure	Mixture	From Fraction 3	Pure	Mixture
A	5.3	1.0	1.4	2.9	0.7	1.9	72.5	73.5	72.5 to 73	130	130.5	130
B	5.5	1.5	2.1	1.9	0.9	1.2	73	73.5	73	129 to 130	130.5	130

ISOLATION AND DETERMINATION

The method employed in removing the oils boiling below 200° C. was to pass steam through 1000-cc. samples of the tar maintained at 150° C. The oil thus separated was distilled over a 14-inch bead column and collected in three fractions—namely, (1) boiling up to 130° C., (2) boiling between 130° and 160° C., and (3) boiling 160° to 190° C.

Fraction 2 was titrated with bromine (in carbon tetrachloride solution), and the styrene content was calculated from the bromine used. The styrene dibromide so formed and recovered by the evaporation of the hydrocarbons other than styrene was found to be practically pure, and amounted to over 95 per cent of the amount calculated from the titration.

Fraction 3 was similarly titrated with bromine, and the indene content calculated from the bromine taken up. The indene was isolated as the oxybromide by gentle steam distillation of the titrated fraction, which removed the other hydrocarbons of the fraction and hydrolyzed the indene dibromide formed during the titration. The crude oxybromide so recovered was approximately equal to that calculated from the amount of bromine used. The purified oxybromide recovery amounted to 60 per cent of the amount calculated from the bromine titration. No other compound was separated from the residual resinous material resulting from the steam distillation of the crude indene dibromide. The writers have always found this resinous material left as a residue when the dibromide is so treated.

IDENTIFICATION

The identification of the styrene was made through the melting point of its dibromide following recrystallization from alcohol, and by the method of mixed melting points. Pure styrene dibromide was prepared from styrene and bromine.

The identification of indene was effected through its oxybromide, which melts at 130° to 131° C. and is otherwise characteristic. Melting points of mixtures of equal parts of the crystals isolated and the oxybromide derivative prepared from indene were taken, and are reported below.

Sample A was a water-gas tar of specific gravity (20° C.) 1.058 and low naphthalene, free carbon, and water content. It was taken from tar storage, and was typical for the plant.

Sample B was a water-gas tar of specific gravity (20° C.) of 1.176, and contained in comparison with Sample A much naphthalene, free carbon, and water. It was taken from the works separator of the plant in which it was produced.

In the table which follows is given the experimental data pertinent to the purpose of the paper. The percentages are all based on 1000-cc. of tar as sampled, and are in terms of volume throughout. The temperatures are corrected values.

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[1] Received June 8, 1923. Published by permission of the Director, U. S. Bureau of Mines.

[2] "Coal Tar and Ammonia," 5th ed., **1916**.

[3] *U. S. Dept. Agr.*, *Bull.* **1036**, 73.

[4] THIS JOURNAL, **6**, 366 (1914).

[5] "Jahrbuch der Hamburgerschen wissenschaftlichen Anstalten," **1893**, p. 132.

[6] Brown, Chairman of Committee on Deposits in Gas Pipes and Meters; "Deposits in Gas Pipes and Meters," American Gas Association, Proceedings Technical Section, **1922**.

The Department of Commerce has announced that after January 1, 1924, "too many asphalt grades" no longer will be the complaint, and that on the date mentioned the recommendations adopted at its recent asphalt paving conference will become effective and the number of asphalt grades for use in the construction of sheet asphalt, asphaltic concrete, asphalt macadam, and surface-treated pavements will be reduced from eighty-eight to nine. The number of asphalt grades used as joint filler in the construction of brick and block pavements and various other types has been reduced from fourteen to four.

The Influence of Hydrogen-Ion Concentration in the Fixation of Vegetable Tannins by Hide Substance[1,2]

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The rate of combination of hide protein with vegetable tannins is a marked function of the hydrogen-ion concentration and of the concentration of the vegetable tannin solution. The results obtained are readily understood in the light of the modern knowledge of the physical chemistry of the proteins and of vegetable tanning extracts. Explanations for changes in behavior with respect to these factors have been offered, based mainly upon the Donnan theory of membrane equilibria, the Procter-Wilson work upon swelling of colloid jellies, the Procter-Wilson theory of vegetable tanning, and the work of Loeb upon proteins.

EVER since 1899, when Hardy[1,*] first defined the isoelectric point, the importance of considering hydrogen-ion concentration when dealing with protein solutions has come increasingly to notice. Procter and Wilson[2] in 1916 explained the changes in swelling of gelatin jellies in acid solutions of different strengths, with and without added salt, by the theory of membrane equilibria which had been published by Donnan[3] in 1911. During the past few years Loeb[4] has made a very complete study of the effect of change in hydrogen-ion concentration and added salt on the physical properties of protein solutions, giving an adequate explanation by means of the Donnan theory for changes in electrical potential difference, viscosity, swelling, and osmotic pressure with change in pH of solution and concentration and kind of added salt.

Since hydrogen-ion concentration has been shown to have such an important bearing on the properties of protein solutions, it was therefore decided to study the effect of changes in hydrogen-ion concentration on the rate of tanning of collagen with various vegetable tan liquors, hoping thereby to throw some light on the nature of this complex reaction.

Materials

In all experiments American standard hide powder was used as the source of hide protein. This was first sifted to remove 100-mesh particles in order to avoid the loss of material fine enough to pass through the filter cloth used in washing, then thoroughly extracted with chloroform to remove fat, and air-dried. The moisture in this stock sample was determined by heating at 100° C. in a vacuum oven for 5 hours, and all weights of hide powder are reported on this moisture-free basis.

As sources of tannin, six different tanning extracts, quebracho, gambier, hemlock bark, oak bark, larch bark, and wattle bark, were employed. A concentrated stock solution of each was prepared by dissolving in water at 85° C. After cooling, insolubles were removed by centrifuging and filtering. Total solids in this clear, concentrated extract were determined by the American Leather Chemists Association method,[5] and all concentrations are reported on the basis of this determination.

Method

The method employed for determination of tannin fixed by the hide powder is essentially that proposed by Wilson and Kern[6] in their modified method, adopting the practical definition of tannin as that material, present in certain vegetable extracts, which is capable of precipitating gelatin from solution, and of forming, with hide protein, a compound that is resistant to washing with water. The Wilson and Kern determination involves simply the measurement of increase in weight of a sample of hide powder, after tanning and thorough washing. For estimation of tannin in an extract by their method, the weight of hide powder and concentration of extract are so chosen as to insure, in 6 hours' contact, complete removal of tannin from the extract as evidenced by a negative gelatin-salt test on the filtrate. Since in the work here recorded it was desired, however, to obtain a comparative measure of the amount of tannin fixed under varying conditions, it was of course necessary to arrange conditions so as to have an excess of tannin in the filtrate in all cases.

In all experiments 2.000-gram samples (dry basis) of the specially purified hide powder were placed in 400-cc. rubber-stoppered bottles. To these were added 100-cc. portions of the tanning extract, and the bottles were rotated for the desired length of time at room temperature in a tumbling machine. The tanned hide powders were then filtered off in Wilson and Kern extractors, using a fine grade of cambric as filter cloth. Samples of the filtrates were saved for later tests, and the hide powders were washed with distilled water until the washings gave a negative test with ferric chloride, thereby indicating the complete removal of tannins and non-tans. The tanned portions of hide powder were air-dried in the extractors and transferred to weighing bottles. The samples were given a preliminary drying for 5 hours at 70° C. in an atmospheric oven, and finally were heated at 100° C. in a vacuum oven for 5 hours. The increase in weight (dry basis) over the original 2.000 grams of anhydrous hide powder represents the amount of tannin fixed.

Filtrates were tested for tannin in every case by the gelatin-salt reagent under the conditions established by Thomas and Frieden,[7] where delicacy may be claimed of at least 1 part of tannin in 100,000 parts of solution.

The older methods for estimation of the tannin content of an extract, by measurement of the change in concentration of the tanning liquor before and after shaking with hide powder, are subject to large errors due to the well-established fact that hide powder removes certain non-tans as well as tannins from tanning solutions, and also to the fact that they fail to take account of changes in concentration due to absorption of water by hide powder from the extract. In the Wilson-Kern method these errors are eliminated, as the adsorbed non-tans are removed in the washing of the tanned hide powder. Moreover, as pointed out by Thompson, Seshachalam, and Hassan,[8] the tanning content of an extract, as determined by the older methods, varies with the acidity of the tanning solution. Wilson and Kern,[9] on the other hand, have shown that their method gives a practically constant tannin value for an extract over a pH range from 3.6 to 7.3.

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[1] Presented before the Division of Leather Chemistry at the 64th Meeting of the American Chemical Society, Pittsburgh, Pa., September 4 to 8, 1922.

[2] Contribution No. 422 from the Chemical Laboratories, Columbia University. Taken from a part of the dissertation submitted by Miss Kelly in partial fulfilment of the requirements for the degree of doctor of philosophy, Faculty of Pure Science, Columbia University, 1923.

[*] Numbers in text refer to bibliography at end of article.

Determination of Proper Concentration

Since it would be necessary in the determination of the influence of hydrogen-ion concentration upon tannin fixation in all cases to be certain of insuring an excess of tannin, in order to have a true measure of the relative amounts of tannin fixed under varying conditions, it was necessary first to establish at what concentration the filtrates would give a positive gelatin-salt test by a study of the concentration curve for each extract for a 24-hour tanning period. The method outlined above was used. The results are summarized in Table I and Fig. 1.

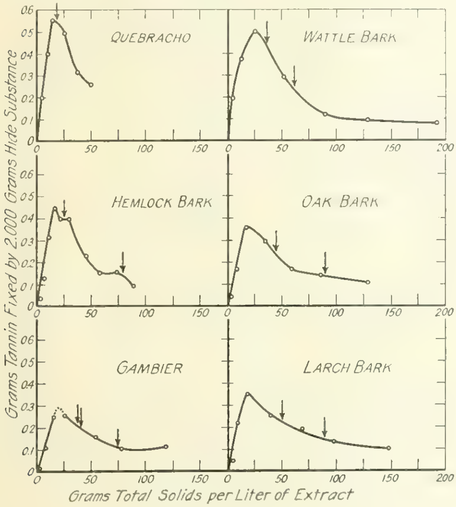

Fig. 1

The arrows in Fig. 1 indicate the concentrations adopted for study of the influence of hydrogen-ion concentration reported later in this paper.

Observation of the curves indicates that all the extracts show a characteristic rise to a maximum, followed by a sharp drop, as the concentration of the extract increases. The maximum point in each case occurs at a concentration of the extract equal to 15 to 25 grams total solids per liter, and is always in the neighborhood of the point at which the first positive gelatin-salt test was obtained on the filtrate.

These results agree very well with those obtained from a similar study of the concentration factor which has been reported from this laboratory.[10] Similar types of concentration curves have been noted by Moeller[11] and by von Schroeder and Paessler[12] for the adsorption of tannic acid by hide substance, who, however, used the older methods for estimation of tannin—i. e., by analysis of an aliquot of the equilibrium solution. Most investigators have confined themselves, however, to a study of adsorption from dilute solution, and as a consequence have reported curves of the usual parabolic form expected for typical adsorption, which, in more extended concentration, experiments show to be erroneous.

The explanation of this typical concentration curve, characterized by a rise to a maximum, followed by a sharp decline, cannot be ascribed to variations of hydrogen-ion concentration of the extract with dilution. The pH of the extracts, measured electrometrically, showed a very slight but regular increase in acidity upon dilution, but the change was too slight to be of any significance here. The explanation must be sought elsewhere. Three different factors are involved:

1—The surface of the hide powder particles, at a concentration of 15 to 20 grams total solids per liter, becomes so heavily tanned that the particles are rendered impermeable to the tanning solution. Consequently, the interior of the particles is relatively unaffected, resulting in a smaller amount of tannin being fixed from the more concentrated solutions. This assumption was offered in 1898 by von Schroeder and Paessler to explain a similar concentration curve obtained by them for the adsorption of tannic acid by hide.

2—A second factor, probably operating to decrease the amount of tannin fixed in a given period of time from the more concentrated solutions, is that, with increasing concentration, an increased aggregation of the tannin particles would be expected, thereby causing a lowered rate of diffusion into the hide substance. Since diffusion into the hide particles must precede fixation, less tannin would be fixed in a given time as a result of this increase in aggregation of particles.

3—Finally, Thomas and Foster[13] have shown for quebracho that the electrical potential difference of the tannin particles against the aqueous phase decreases with increase in concentration of the tanning solution. Probably this latter factor is the more important one in retardation of tanning upon increase of concentration of the extract, since, as will be shown later, anything which effects a reduction of the potential difference at the surface of the tannin particles will cause a decrease in the rate of tanning. Moreover, concomitant with increasing concentration of the extract there is a higher concentration of non-tans. And since these non-tans diffuse much more rapidly into the hide substance than do the tannins, owing to their lower molecular weight, their effect would tend to counteract the retardation due to heavy surface tannage and aggregation of the tannin particles.

Effect of Change of pH of the Tanning Solution

Having determined a suitable concentration for use in the pH series of experiments, by the preliminary study of the concentration factor, as described above, 100-cc. portions of the extract to be studied were prepared in which the pH values varied from 1.0 to 11.0. The adjustment to the desired concentration of hydrogen ion was made by addition to the given amount of stock solution, before dilution to 100 cc., the required amount of 0.5 *M* hydrochloric acid or 0.5 *M* sodium hydroxide, previously determined by electrometric titration of a sample of the extract. Considerable difficulty was experienced in the titration of the tan liquors in the pH range from 6.0 to 8.0, due probably to reduction potentials.

Table I—Effect of Concentration upon Fixation of Tannin

Grams Totals Solids per Liter Extract	Grams Tannin Fixed by 2 Grams Hide Powder	Reaction of Filtrate with Gelatin-Salt Reagent	Grams Total Solids per Liter Extract	Grams Tannin Fixed by 2 Grams Hide Powder	Reaction of Filtrate with Gelatin-Salt Reagent
Quebracho (pH = 4.6)			*Wattle* (pH = 4.2)		
5.01	0.196	−	5.12	0.197	−
10.03	0.400	Very slightly +	12.8	0.378	−
15.04	0.546	+	25.6	0.498	+
25.07	0.482	+	51.2	0.289	+
37.6	0.316	+	89.6	0.121	+
50.1	0.263	+	128.0	0.094	+
			192.0	0.084	+
Hemlock (pH = adjusted to 5.0)			*Larch* (pH = 3.8)		
			3.95	0.045	−
3.36	0.036	−	9.87	0.226	−
6.64	0.136	−	19.74	0.353	slightly +
11.15	0.315	−	39.48	0.259	+
16.00	0.448	−	69.09	0.185	+
21.81	0.388	+	98.70	0.134	+
29.75	0.385	+	148.1	0.103	+
46.06	0.230	+			
58.57	0.157	+			
73.94	0.167	+			
88.72	0.089	+			
Oak (pH = 4.0)			*Gambier* (pH = 4.7)		
3.38	0.045	−	3.13	0.015	−
8.45	0.171	−	7.83	0.107	−
16.90	0.363	−	15.7	0.253	+
33.80	0.300	+	31.4	0.262	+
59.21	0.187	+	54.8	0.162	+
84.50	0.131	+	78.5	0.103	+
126.8	0.114	+	117.7	0.119	+

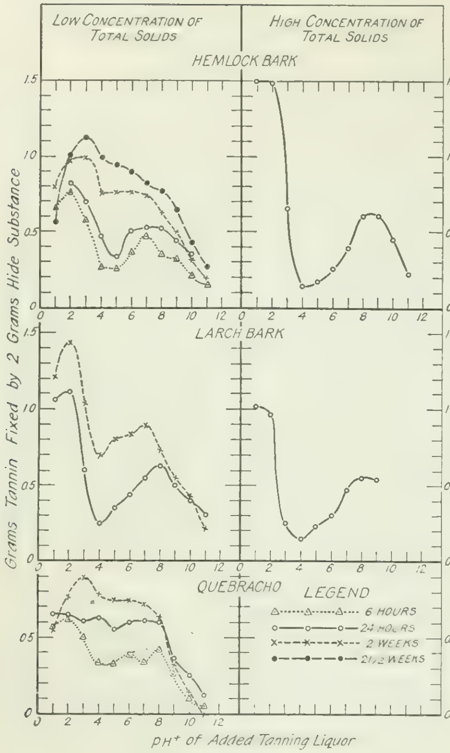

Fig. 2

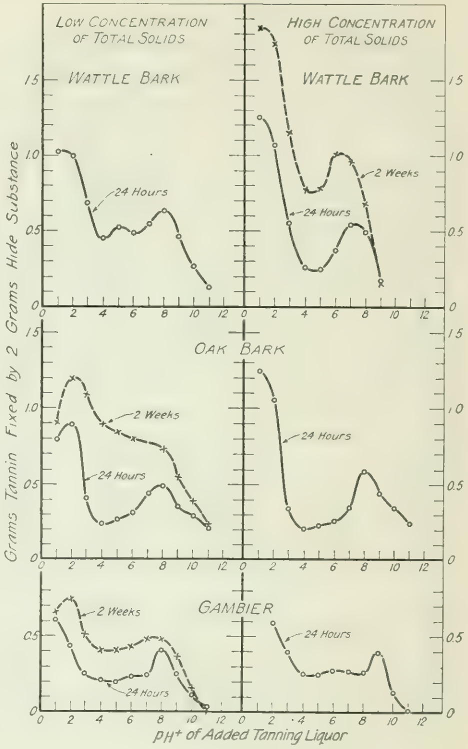

Fig. 3

Attempts were made in the earlier experiments to measure the pH of the tanning solution in equilibrium with the tanned hide powder at the end of the tanning period, since this value, of course, is the one of real significance in the Donnan effect. The measurements were attended with such great difficulty, due to electrode effects, that the results obtained were exceedingly unreliable, and in the range of pH from 6.0 to 8.0, were absolutely impossible to measure. Oxidation during the "drumming," especially in the alkaline range, probably results in the establishment of a reduction potential when measurements of the pH of the equilibrium solution by means of the hydrogen electrode are attempted.

Table II Change in pH of Hemlock Bark Extract. 24 Hour Tanning Period

A—Untreated Extract

Original solution	2.0	3.0	4.0	5.0	6.0	7.0	8.0		
Equilibrium solution	2.2	3.2	4.0	4.7	(impossible to measure)				

B—Clarified Extract

Original solution	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Equilibrium solution	2.9	3.8	4.3	4.9	(impossible to measure)			7.7	8.8

The use of buffer solutions was precluded since, as will be shown later herein and in a separate paper, the presence of salts influences the fixation of tannin to a remarkable degree. It should be noted that tanning solutions themselves show considerable buffer action in the acid range, due to the tannic acids present. Since it is believed that the Donnan effect is only responsible for the initial rate of tanning, while, from the practical point of view, the question of pH of the original solution is the most important one, the attempt to measure equilibrium pH values was abandoned.

The study was extended to include the fixation of tannin at different concentrations of hydrogen ion from each of the six extracts by the method previously described, at two different concentrations of each extract, except quebracho, and for different time intervals, as shown in Table III and Figs. 2 and 3.

Table III—Effect of Change in pH of Tanning Solution upon Fixation of Tannin

Hemlock Bark Extract

	Total Solids = 24.0 Grams per Liter				Total Solids = 70.6 Grams per Liter
pH of Tanning Solution	Grams Tannin Fixed by 2 Grams Hide Powder in				Grams Tannin Fixed by 2 Grams Hide Powder in
	6 Hours	24 Hours	2 Weeks	21.5 Weeks	24 Hours
1.0	0.653	...	0.687	0.557	1.494
2.0	0.756	0.812	0.889	1.020	1.478
3.0	0.570	0.686	0.921	1.119	0.657
4.0	0.273	0.466	0.694	0.995	0.134
5.0	0.261	0.330	0.703	0.940	0.174
6.0	0.367	0.495	0.698	0.894	0.265
7.0	0.478	0.520	0.675	0.825	0.385
8.0	0.353	0.519	0.570	0.767	0.605
9.0	0.318	0.438	0.438	0.635	0.601
10.0	0.215	0.346	0.249	0.419	0.449
11.0	0.155	...	0.119	0.269	0.223

Oak Bark Extract

	Total Solids = 42.3 Grams per Liter		Total Solids = 88.2 Grams per Liter
pH of Tanning Solution	Grams Tannin Fixed by 2 Grams Hide Powder in		Grams Tannin Fixed by 2 Grams Hide Powder in
	24 Hours	2 Weeks	24 Hours
1.0	0.796	0.901	1.248
2.0	0.891	1.187	1.056
3.0	0.411	1.088	0.343
4.0	0.242	0.888	0.208
5.0	0.267	0.840	0.229
6.0	0.306	0.796	0.255
7.0	0.439	0.725	0.349
8.0	0.477	0.548	0.599
9.0	0.359	0.385	0.442
10.0	0.284	0.337	0.346
11.0	0.210	0.236	0.237

TABLE III—(*Concluded*)

Quebracho Extract

TOTAL SOLIDS = 18.3 GRAMS PER LITER

pH of Tanning Solution	Grams Tannin Fixed by 2 Grams Hide Powder in 6 Hours	24 Hours	2 Weeks
1.0	0.568	0.665	0.564
2.0	0.622	0.644	0.770
3.0	0.498	0.612	0.888
4.0	0.344	0.631	0.777
5.0	0.332	0.553	0.743
6.0	0.380	0.596	0.744
7.0	0.333	0.613	0.715
8.0	0.417	0.599	0.625
9.0	0.269	0.366	0.316
10.0	0.100	0.258	0.140
11.0	0.050	0.120	(−0.025)

Wattle Bark Extract

	TOTAL SOLIDS = 36.9 GRAMS PER LITER	TOTAL SOLIDS = 61.4 GRAMS PER LITER	
pH of Tanning Solution	Grams Tannin Fixed by 2 Grams Hide Powder in 24 Hours	Grams Tannin Fixed by 2 Grams Powder in 24 Hours	2 Weeks
1.0	1.034	1.255	1.840
2.0	0.995	1.073	1.743
3.0	0.681	0.548	1.152
4.0	0.451	0.258	0.769
5.0	0.521	0.250	0.784
6.0	0.481	0.376	1.006
7.0	0.549	0.538	0.957
8.0	0.630	0.476	0.680
9.0	0.473	0.175	0.151
10.0	0.272	... [a]	...
11.0	0.131	...	...

[a] Points omitted due to uncertain titration values with hydrogen electrode.

Larch Bark Extract

	TOTAL SOLIDS = 49.4 GRAMS PER LITER		TOTAL SOLIDS = 98.8 GRAMS PER LITER
pH of Tanning Solution	Grams Tannin Fixed by 2 Grams Hide Powder in 24 Hours	2 Weeks	Grams Tannin Fixed by 2 Grams Hide Powder in 24 Hours
1.0	1.067	1.212	1.014
2.0	1.111	1.443	0.970
3.0	0.597	1.038	0.250
4.0	0.248	0.694	0.150
5.0	0.355	0.798	0.229
6.0	0.441	0.825	0.303
7.0	0.548	0.890	0.475
8.0	0.627	0.727	0.551
9.0	0.501	0.554	0.540
10.0	0.416	0.421	...
11.0	0.303	0.214	...

Gambier Extract

	TOTAL SOLIDS = *39.7 †37.8 GRAMS PER LITER		TOTAL SOLIDS = 76.5 GRAMS PER LITER
pH of Tanning Solution	Grams Tannin Fixed by 2 Grams Hide Powder in *24 Hours	†2 Weeks	Grams Tannin Fixed by 2 Grams Hide Powder in 24 Hours
1.0	0.796	0.657	...
2.0	0.891	0.744	0.586
3.0	0.411	0.510	0.393
4.0	0.242	0.408	0.258
5.0	0.267	0.412	0.249
6.0	0.306	0.427	0.275
7.0	0.439	0.476	0.272
8.0	0.477	0.477	0.266
9.0	0.359	0.368	0.391
10.0	0.284	0.155	0.125
11.0	0.210	(−0.011)	0.006

An examination of the curves shows certain characteristics with change in pH of the tanning solution:

1—A minimum is always obtained in the neighborhood of pH of 5.0.

2—The curves rise from this minimum at 5.0 to a maximum at pH of 2.0 to 3.0 on the acid side, and to a maximum at pH of 7.0 to 8.0 on the alkaline side of this minimum, beyond which there is a drop in each case. In the concentrated solutions in the more acid range, the mass effect of the increased concentration of tannin is manifested by an increased fixation of tannin.

3—With high concentrations of the extract, the minimum at pH of 5.0 is even more marked than with the more dilute solutions, as would be expected from the results shown in the concentration curves, and there is usually a considerably greater amount of tannin fixed at corresponding pH values during identical time periods.

It will be recalled that the isoelectric point of collagen (hide powder, to be exact) has been established as at pH of 5 by work in this laboratory[14] using the dye fixation method, and by Porter[15] in England using degree of swelling. The work of Porter, who studied the swelling of hide powder over a pH range from −0.3 to 13.9, showed a minimum at pH of 4.8, while maxima appeared at pH of 2.2 and pH of 12.5. Wilson and Gallun,[16] in a study of the plumping of calfskin at 7° C. as a function of concentration of hydrogen ion, observed two minimum points of plumping at pH of 5.1 and 7.6, respectively, and they suggest that these two points of minimum represent the isoelectric points of two different forms of collagen, which undergoes a change of form, possibly an internal rearrangement, in passing from acid to alkaline solution. Wilson and Kern[17] also observed a similar unexpected phenomenon for the swelling of gelatin at 7° C., one minimum at the generally accepted isoelectric point, pH of 4.7, and another at pH of 7.7. It is further to be noted that Thomas and Foster[18] have shown that vegetable tannin particles are amphoteric in character, with isoelectric points from 2.0 to 2.5, being negatively charged when the hydrogen-ion concentration falls below this figure and positively charged in more acid solutions. All these factors are involved in an explanation of the curves obtained.

MECHANISM OF TANNING

Various theories have been put forward from time to time to explain the mechanism of tanning. Seguin (1796)[19] recognized that tanbark contained a "particular principle" which was soluble in water and gave a precipitate with gelatin, and he pointed out that this principle fixed itself upon the hide in tannage, effecting a "specific combination" between the tanning material and the hide. Knapp (1858)[20] considered tanning to result from a precipitation of the tanning material upon the fibers of the hide, resulting in a protective coating. This theory has been generally discarded, although Moeller[11] has recently revived the idea. The present-day theories are of two main types—one viewpoint being that tanning is a purely physical adsorption following the Freundlich adsorption isotherm, the other regarding tanning as of a chemical nature. Two important chemical theories have been advanced, one based upon the modern conceptions concerning the physical chemistry of the proteins, the other involving oxidation reactions of complex organic compounds.

PHYSICAL-CHEMICAL THEORY—This viewpoint rests upon the conception that proteins are amphoteric electrolytes capable of reacting to form salts with either acids or bases, according to the hydrogen-ion concentration of the solution in which the protein is placed, the isoelectric point being that point between these two regions at which ionization values of the protein, as base and acid, are equal and at a minimum. Starting with this viewpoint and employing the Donnan theory of membrane equilibria,[3] Procter[21] in 1914 and Procter and Wilson[2] in 1916 were able to explain quantitatively the swelling of gelatin jellies in acid solution, while in 1918,[22] by a more general treatment, the theory was extended to include the explanation of swelling of any colloid jelly. Loeb,[4] working with gelatin, casein, and egg albumin, has extended the work to explain the other properties characteristic of colloidal behavior—viz., electrical potential difference, viscosity, osmotic pressure, and stability. All these properties are a function of the hydrogen-ion concentration of the protein solution and of the valency of the ion in combination with the protein. The curves, in which the values for any of the above-mentioned properties are plotted against the pH values of the equilibrium solution, exhibit points of minima at the pH corresponding to the isoelectric point of the protein, rising rapidly to maxima on either side as the pH of the solution moves away from the isoelectric point, and again falling off as the distance from the isoelectric point is further increased. For all monovalent ions in combination with the protein, maximum values for any given property are identical, while for all divalent ions a lower maximum value is obtained, but at the same pH value for the equilibrium solution. Moreover, added neutral salt always effects a reduction in value of the property in question—e. g., swelling, potential difference, etc.—while increase in the amount of protein causes an increase in value of the property under consideration, providing that the concentration of hydrogen ion of the protein solution remains unchanged. The addition of nonelectrolytes is without effect on the value of the given property. The Donnan theory furnishes a complete and satisfactory explanation of this behavior, as has been shown by Procter and Wilson and by Loeb. This theory, based upon thermodynamic reasoning, predicts the equilibrium conditions which will arise in a system in which a membrane separates two solutions of electrolytes, one of which contains one ion which cannot diffuse through the membrane, while all other ions are readily diffusible. The result is an unequal distribution of the diffusible ions on the opposite sides of the membrane, such that, at equilibrium, the products of the concentrations of each pair of oppositely charged diffusible ions are the same for opposite sides of the membrane. As a necessary result of this unequal distribution of ions at equilibrium, there is developed an electrical potential difference which should have a minimum value at the hydrogen-ion concentration corresponding to the isoelectric point of the protein, and should exhibit maximum values, followed by a decline as the hydrogen-ion concentration of the solution is either increased or decreased from the isoelectric point. Moreover, this excess concentration of diffusible ions gives rise to osmotic pressure and, if we are dealing with a jelly, causes swelling.

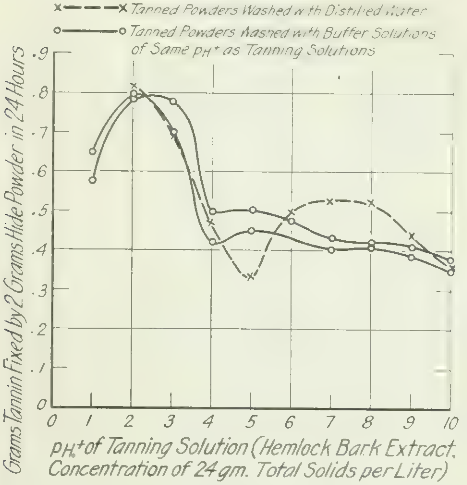

FIG. 4

The Procter-Wilson[23,24] theory of tanning is based upon this physico-chemical point of view. Collagen, when placed in a slightly acid solution, such as is commonly employed in tanning operations, is prevented from diffusing by its jelly-like character. Consequently, a Donnan equilibrium is set up which results in the establishment of a potential difference between the positively charged collagen and the solution. If all other factors are kept constant, the magnitude of this potential difference will depend upon the acidity of the solution. Likewise, each tannin particle is negatively charged. There is of necessity a resulting tendency of these opposite charges to neutralize each other, which is measured by the sum of their absolute values. It is this potential difference which is believed to provide the mechanism that brings the tannin particles into intimate contact with the collagen, and is therefore the most important factor in the control of the initial rate of tanning.

OXIDATION REACTIONS—A second chemical viewpoint is that tanning is the result of oxidation between quinone-like bodies present in the tanning solution and amino groups in the collagen molecule. The chief exponents of these oxidation theories, which are as yet very imperfectly understood for vegetable tanning, have been Meunier,[25] Fahrion,[26] and Powarnin.[27]

With this in mind, the rise in the curves in the acid range from the minimum at pH = 5.0 to the maximum at about pH = 2.0 is readily understandable from the viewpoint of the Procter-Wilson theory. The curves parallel the swelling curves of Porter[15] for collagen, and Loeb's work[4] with gelatin has demonstrated that changes in swelling and potential difference are practically coincident, each showing a minimum at the isoelectric point of the protein and maxima at identical pH values on either side of the isoelectric point. We should therefore expect collagen to be positively charged in this range of pH values, with a minimum potential difference at pH = 5.0, and a gradual increase in potential difference as the pH decreases to 2.0. Consequently, the reaction of the positively charged collagen with the negatively charged tannin particles should exhibit a minimum rate of fixation at pH = 5.0 and an increase in fixation from 5.0 to 2.0. It is rather surprising, however, to find that tannin is fixed on both sides of the isoelectric point of collagen (5.0) since it has been generally conceded that tanning could take place only in acid solution. Moeller[28] reported that adsorption of quebracho extract by hide powder was increased when acid was added to the tanning solution, but that practically no adsorption took place in alkaline solution. In the discovery by Wilson and Gallun[16] of two points of minimum swelling for calfskin, at pH = 5.0 and 7.7, respectively, we have a possible explanation of fixation through part of this alkaline range. Assuming two forms of collagen and an intramolecular change in this region resulting in an equilibrium between the one form, *A*, stable in acid solution and with an isoelectric point at pH = 5.0, and the other form, *B*, stable in alkaline solution and with an isoelectric point at pH = 7.7, it follows that, with increasing amounts of *B*, positively charged, in the solution, as the pH increases from 5.0 to 7.7 reaction will naturally take place at an increasing rate with the negatively charged tannin particles. The Procter-Wilson theory furnishes, therefore, a satisfactory working hypothesis for tannin fixation in the pH range from 2.0 to 7.7.

It is to be noted, however, that beyond the maximum points of fixation at pH of approximately 2.0 and 7.7, respectively, the curves show clearly that very definite tannin fixation has taken place, although there is considerable falling off in the rate of tanning. The Procter-Wilson theory fails to account for fixation at these extremes of pH, since the electrical charges on the collagen and tannin particles are identical in sign in these areas, both being positively charged at a pH below 2.0, and both being negatively charged at a pH above 8.0. The question arises whether this fixation is not merely an apparent one, due to change in pH during washing of the tanned powders with distilled water, whereby the tanning solution might have been fixed through removal of acid or alkali by the distilled water before being completely removed itself; but this question has been effectively answered by several experiments in which both tanning and washing solutions were at identical pH values, as shown below.

Experiments were run in which 2.000-gram samples (dry basis) of hide powder were tanned for 24 hours with 100-cc. portions of tanning solution of definite pH. The tanned powders were then transferred to the Wilson-Kern extractors and each sample was washed with a buffer solution, whose pH, by electrometric titration, had been made identical with that of the original tanning solution, this washing being continued until uncombined tannin had been completely removed, as evidenced by a negative gelatin-salt test on the filtrate. The washing was then continued with distilled water until the buffer solution, in turn, had been completely removed, as well as non-tans. The samples were finally dried and weighed in the usual fashion for determination of tannin fixed.

Results of the average of two duplicate sets of values obtained by this method are recorded in Table IV and Fig. 4, and the average values for tannin fixed are given, together with the corresponding values obtained in an earlier experiment where the washing was done with distilled water in the usual fashion.

TABLE IV—EFFECT OF NATURE OF WASHING SOLUTION

pH of Tanning Solution	WASHING SOLUTION EMPLOYED	GRAMS TANNIN FIXED BY 2 GRAMS HIDE POWDER WASHED With Buffer Solutions	With Distilled Water
1.0	HCl (approx. 0.1 *M*)	0.613	...
2.0	HCl (approx. 0.01 *M*)	0.790	0.812
3.0	HCl (approx. 0.001 *M*)	0.742	0.686
4.0	HCl (approx. 0.0001 *M*)	0.458	0.466
5.0	Mixtures of *M* /15 primary potassium and secondary sodium phosphates	0.478	0.330
6.0		0.476	0.495
7.0		0.417	0.520
8.0		0.409	0.519
9.0		0.400	0.438
10.0	NaOH (approx. 0.001 *M*)	0.362	0.346

Since a comparison value at pH of 1.0 was lacking in this set, the following values were obtained, using wattle bark extract at pH of 0.9, the values being run in duplicate:

TABLE V—EFFECT OF NATURE OF WASHING SOLUTION

WASHING SOLUTION EMPLOYED	Grams Tannin Fixed by 2 Grams Hide Powder
Distilled water	0.987
HCl (pH = 0.9; approx. 0.1 *M*)	0.739

An examination of these results shows that the curves obtained upon washing with buffer solutions parallel closely the one obtained upon washing with distilled water in the range from pH of 2.0 to 4.0, where hydrochloric acid of low concentration was employed, and again at pH of 10.0, where 0.001 *M* sodium hydroxide was used. At pH of 1.0, where the concentration of hydrochloric acid used for washing was approximately 0.1 *M*, the fixation was slightly lowered, but real values, both for hemlock and wattle extracts, were obtained for tannin fixed. In the range from 5.0 to 9.0, where mixtures of *M*/15 phosphate solutions were used in washing the tanned powders, the variations from the normal pH curve are merely due to a salt effect, showing an increase in fixation at pH of 5.0, and a decrease from pH of 7.0 to 9.0, similar in every way to the changes produced where salts are added to the tanning liquors prior to addition to the hide powders, which will be discussed in a separate paper.

It can safely be concluded, therefore, that the fixation of tannin at pH values of 1.0 to 2.0, and 8.0 to 10.0 is a real and not an apparent one, and consequently that some other factor, possibly oxidation reactions, in addition to the coprecipitation of oppositely charged colloidal particles, contributes to the fixation of vegetable tannins by collagen.

Evidence for a difference in kind of fixation of tannin in alkaline solutions as compared to that in acid solutions, shown by alcohol extraction of the tanned leathers, will be described in a later paper.

TIME FACTOR IN FIXATION OF TANNIN

From the foregoing tables and graphs, the effect of the time factor on fixation of tannin by hide powder may be observed. The time effect may be best studied with the family of curves obtained with hemlock extract, where the fixation from the more dilute solution, with changing pH, was studied for time intervals of 6 hours, 24 hours, 2 weeks, and 21.5 weeks. The characteristic minimum at pH = 5.0, obtained in the shorter periods, is gradually eliminated, being hardly noticeable in the 2 weeks' tanning period and completely disappearing in 21.5 weeks. The amount of tannin fixed is always greater with increasing time, but while the minimum at 5.0 disappears, the maximum at 2.0 to 3.0 is steadily maintained, thus indicating that not only is fixation of higher rate at this optimum acidity, but of higher absolute attainment as well. From the data given in Table III it is evident that equilibrium has almost been reached in 21.5 weeks at pH of 2.0 and 10.0 to 11.0, but has been only approximately attained at the other pH values. Furthermore, it is interesting to observe that, with the more astringent extracts, the flat type of pH curve is reached in dilute solution in a fairly short tanning period—e. g., 2 weeks with quebracho.

The question as to the extent to which hydrolysis may have been responsible for the curves has also been investigated. For a tanning period of 24 hours, analysis of the original extract and of aliquot portions of the filtrate for nitrogen by the Kjeldahl method showed no hydrolysis at pH = 1 to pH = 8, a trace at pH = 9, and 1.7 per cent hydrolysis of the hide powder at pH = 10. For the 21.5-week period, with the less concentrated hemlock extract, in which hydrolysis would have most opportunity to show its effect, a similar analysis of the filtrates showed that only at the extremes of pH (1.0 and 11.0) was there sufficient hydrolysis to account for the drops in the curve, as follows:

pH of tanning solution	1.0	3.0	5.0	9.0	11.0
Per cent hydrolysis	20.6	0.29	0.18	1.86	4.22

It is apparent that except for the extremes of acidity or alkalinity in the long time experiment above, the question of hydrolysis affecting the results reported may be excluded as of no significance.

ACKNOWLEDGMENT

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Conditions Affecting the Hydrolysis of Collagen to Gelatin[1]

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Conditions affecting the hydrolysis of collagen to gelatin and of gelatin to its degradation products have been studied and the results tabulated and discussed. The conditions studied include hydrogen-ion concentration, presence of salts, temperature, duration of heating, ratio of stock to water, agitation, condition of stock, and the plumping reagent.

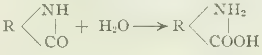
The evidence upon the constitution of collagen and its relation to gelatin has been discussed, and the findings of the present report brought to bear upon this problem, indicating that collagen is not a simple anhydride of gelatin, but rather a polarization complex produced by chemical condensation.

THERE has been but little work reported dealing with the hydrolysis of collagen. Hofmeister[2] as far back as 1878 regarded the change of collagen to gelatin as a simple hydration, one molecule of water being added to each molecule of collagen:

$$\underset{\text{Collagen}}{C_{102}H_{149}O_{38}N_{31}} + H_2O \rightleftharpoons \underset{\text{Gelatin}}{C_{102}H_{151}O_{39}N_{31}}$$

He regarded collagen, therefore, as a simple anhydride of gelatin, and considered the reaction as reversible, since, on heating the gelatin to 130° C., he believed he obtained a regeneration of the collagen. This material was much less soluble than gelatin, but Alexander,[3] and also Emmett and Gies[4] have contended that the conversion of collagen to gelatin was more complex and not reversible. The latter investigators found that, whereas collagen was not attacked by trypsin, yet normal gelatin and also dehydrated (at 130° C.) gelatin were readily attacked by that enzyme. They also reported that ammonia was evolved upon heating collagen in water, while this did not occur upon a similar treatment of gelatin.

Plimmer[5] believes that the difference in the action of pepsin and trypsin lies in the ability of the former, and the inability of the latter, to open up an anhydride ring. He thinks that all proteins which are resistant to the action of trypsin until they have been acted upon by pepsin "have all their units contained in the anhydride ring." Thus, the conversion of collagen to gelatin might be represented:



$$R\left\langle\begin{matrix} NH \\ | \\ CO \end{matrix}\right. + H_2O \longrightarrow R\left\langle\begin{matrix} NH_2 \\ | \\ COOH \end{matrix}\right.$$

Collagen Gelatin

The present investigation was undertaken in the hope that further light might be found which would indicate the nature of the conversion into gelatin, and more particularly to study the several conditions affecting the hydrolysis. The procedure adopted involved an hydrolysis in water or other electrolyte for a definite period at a definite temperature. The distribution of the nitrogen between that recovered in the solution, that evolved as ammonia during hydrolysis, and that remaining in the residue, was determined. The amino nitrogen was determined as one means of checking the extent to which the gelatin molecule had been degraded during the hydrolysis. The H-ion concentration was determined electrometrically in the solution. The viscosity and jelly consistency were also determined as further checks on the degree of hydrolysis that had taken place.

EXPERIMENTAL

The stock used throughout the greater part of these experiments consisted of well-limed hide pieces. The liming had been carried out at the glue factory in the usual way by soaking the hide cuttings in milk of lime, with occasional changes, for about 10 weeks. It was kept in the cooler and used as required. Except as especially noted below, the stock, preparatory to use, was washed several times in water at about 15° C. until all dirt, hair, and lime that could be removed had been freed from the stock. The fatty portions on the inner surface were removed and the trimmings cut into uniformly sized pieces of about 2 x 1/2 x 1/2 inches. These were then ready for the hydrolysis. The water content and the total nitrogen by a modified Kjeldahl method were determined as these values were necessary for the final calculations.

Five hundred grams of stock prepared as above were weighed into a 2-liter flask and 800 cc. of distilled water (or other solution) at 80° C. added. The flask was at once placed in a water-oil thermostat regulated to a temperature of 80° C. ±0.1°. Air, purified by passing through a solution of potassium hydroxide and saturated with water by passing through water at 80° C., was caused to bubble slowly through the flask and then passed through a measured quantity of standard 0.1 *N* hydrochloric acid. By a subsequent titration any ammonia evolved during the hydrolysis was determined. The flask was allowed to remain undisturbed for exactly 8 hours, at the end of which period the solution was strained through a 100-mesh sieve and put in the cooler until the following day. The residue was in some cases examined for water and nitrogen content to find the nitrogen unrecovered, but this procedure was found to check that found by difference between 100 and the nitrogen recovered in solution plus the nitrogen evolved as ammonia, and so was discarded.

The solution was placed in a water thermostat regulated to 35° C. ± 0.03°, and all measurements were made at that temperature. The total nitrogen of the solution was determined by a modified Kjeldahl method, and recorded as percentage of the total nitrogen of the original stock recovered in solution. The amino acid nitrogen was determined by both the nitrous acid method of Van Slyke[6] and the formaldehyde titration method of Sörensen.[7] The former method gave results a little higher than the latter in most instances.

The hydrogen-ion concentration was determined by the use of the hydrogen electrode, using the apparatus of Clark[8] and a 0.1 *N* potassium chloride calomel half cell. A potentiometer was employed.

The viscosity was measured at 35° C. by means of an Ostwald capillary-tube viscometer, and expressed as seconds of outflow (since relative results only were desired). The jelly consistency was measured by an improved instrument of the Lipowitz[9] type. The solution was placed in a closed jar 4 x 1.5 inches, and set in the cooler at 5° C. for 24 hours. The pressure necessary to force a $^3/_8$-inch glass rod through the surface was measured and this expressed as grams.

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[1] Received June 9, 1923. Presented at the First National Symposium on Colloid Chemistry, Madison, Wis., June 12 to 15, 1923.

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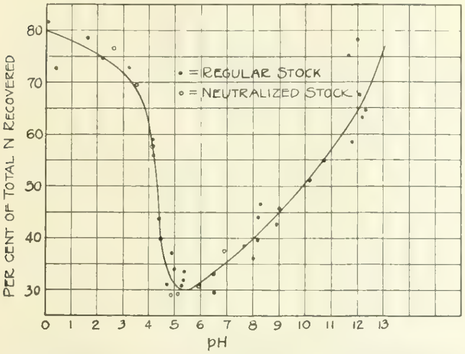

FIG. 1—EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON THE PERCENTAGE OF THE TOTAL NITROGEN RECOVERED IN THE SOLUTION

VARYING HYDROGEN-ION CONCENTRATION

In the first series the solutions added to the stock consisted of dilute hydrochloric acid, water, and sodium hydroxide of such concentrations that the final solution as recovered varied in H-ion concentration from pH 0.1 to pH 12.4. About thirty-five runs were made, so that the interval in pH between different runs was in all cases slight.

In Figs. 1 to 5 are plotted the curves for the several determinations. In each case the pH is indicated on the abscissa. The ordinates represent, in Fig. 1, the percentage of the total nitrogen recovered in the solution; in Fig. 2, the percentage of the total nitrogen evolved as ammonia; in Fig. 3, the percentage of the nitrogen of the solution which is in the form of terminal amino groups; in Fig. 4, the viscosity of the solution at 35° C. expressed in seconds of outflow through an Ostwald viscometer; and in Fig. 5, the jelly strength of the gel at 5° C. in grams.

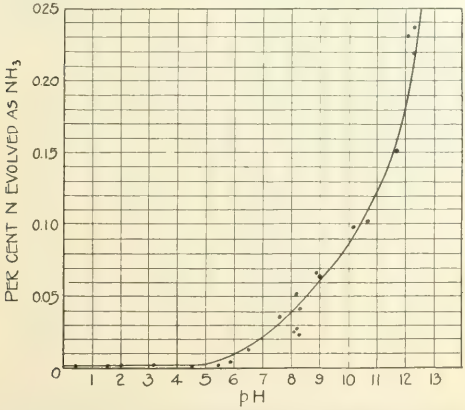

FIG. 2—EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON THE PERCENTAGE OF NITROGEN EVOLVED AS NH_3

The figures bring out a few points which should be emphasized. In the first place, there is a great deal of fluctuation from the mean curves which may be drawn from the data. A single test at any point means very little, and it is only by the accumulation of a considerable number of analyses that we are permitted to draw representative curves. This is due to the irregularity, in spite of care in selection, of the stock employed, and of its water and nitrogen content. But from the large number of data in hand we are justified in making specific conclusions.

Fig. 1 shows that when the concentration of acid in the hydrolyzing mixture is such as to bring the acidity of the final solution to about pH 5 or 6, the hydrolysis is least, only about 30 per cent of the nitrogen of the stock passing into solution under the conditions of the experiment. At slightly stronger concentrations of acid the hydrolysis increases markedly, and it also increases, but less rapidly, with increasing alkalinity.

Fig. 2 shows that up to a pH of 5.4 there is practically no evolution of ammonia, as of course would be expected, but that above pH 5.4 ammonia is evolved in amounts increasing rapidly with the alkalinity of the solution.

Fig. 3 indicates the extent of the secondary hydrolysis—namely, the breaking down of the gelatin molecule into its degradation products, proteose, peptone, and amino acids. Throughout the range of pH 3 to 8 this secondary hydrolysis is slight, but beyond either of these limits, and especially at moderately high alkaline concentration, as pH 12, it becomes very important.

The variation in viscosity with pH of hydrolyzing solution is shown in Fig. 4. There is indicated a distinct minimum at pH 4.7 and a maximum at pH 7.5 to 8.0. There is also a lesser high point at pH 4.1.

The jelly strength curve shown in Fig. 5 is very similar to the viscosity curve.

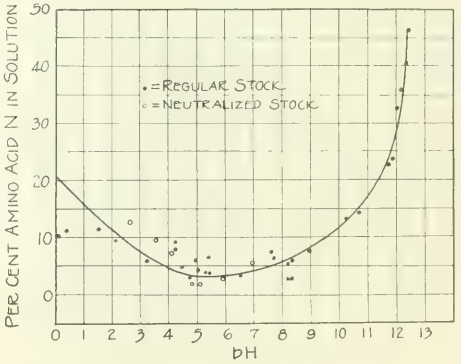

FIG. 3—EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON THE PERCENTAGE OF AMINO ACID NITROGEN RECOVERED IN THE SOLUTION

INFLUENCE OF SALTS

It seemed possible that the excess of lime which remained in the stock after the washing as usually carried out might influence the results, and a number of runs were made following a special preliminary treatment. The stock was first washed several times with cold water, and then placed in a ball mill with a solution of about 0.01 *N* hydrochloric acid. This washing was followed again by a washing in water. This left the stock practically neutral, as shown by the fact that an hydrolysis in pure water gave a final solution of pH 6.9.

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Different amounts of concentrated hydrochloric acid were then introduced into hydrolyzing solution and runs made as before. There was no observable variation in the resulting data until the acidity of the final solution showed a pH of about 4.1. From pH 4.1 to pH 2.6 the solution showed a higher viscosity and jelly strength than the previous tests of similar acidity, but the amount of nitrogen recovered and the degree of the secondary hydrolysis were not noticeably altered. Ammonia was not determined in this series.

The difference in the curves for viscosity and jelly strength are shown by the dotted lines in Figs. 4 and 5.

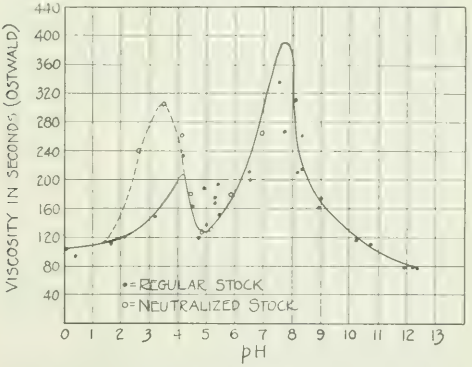

FIG. 4—EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON VISCOSITY OF PRODUCT AT 35° C.

INFLUENCE OF TEMPERATURE

Having established the general direction and nature of the several curves illustrative of the hydrolysis, it seemed very desirable to determine the influence which a number of other factors exerted in the process. The influence of temperature was determined by making the runs at 70°, 90°, and 95° C. at seven different H-ion concentrations each. The period of heating was 8 hours. The stock was washed with acid as described above, since the results were found to be more uniform by that procedure. Only the total nitrogen recovered in the solution and the amino acid nitrogen of the solution were determined, since these data defined with reasonable completeness the progress of the hydrolysis.

Fig. 6 shows the percentage of nitrogen recovered in solution plotted against the pH of the final solution, for the four temperatures studied. The 80° C. curve is drawn in from Fig. 1. The general type of curve remains much the same throughout, but the depression at pH 5.5 becomes less exaggerated at the higher temperatures.

In Fig. 7 the amino acid nitrogen of the solution is plotted against the pH for the several temperatures, the 80° C. curve being drawn in from Fig. 3.

INFLUENCE OF PERIOD OF HEATING

A series of runs was made at seven different H-ion concentrations, tests being made for total nitrogen recovered in solution and amino nitrogen of the solution at intervals of 6, 12, 24, 72, and 168 hours. The temperature was in all cases 80° C. Fig. 8 shows the curves for the nitrogen recovered in solution plotted against the pH of the final solutions for the several periods of heating. The curve for the 8-hour period is drawn in from Fig. 1. At 72 hours the curve is nearly straight, but at 168 hours a depression occurs on the alkaline side. This is probably due to the loss of an appreciable quantity of nitrogen as ammonia under those conditions.

In Fig. 9 the amino acid nitrogen of the solution is plotted against the pH for the several periods of heating, and the curve for the 8-hour period drawn in from Fig. 3. At 72 hours from 70 to 80 per cent of the nitrogen of the solution is amino acid nitrogen, and at 168 hours it reaches its maximum at 92 per cent and drops on the alkaline side. This drop is also probably due to the formation of ammonia.

INFLUENCE OF RATIO OF STOCK TO WATER

Throughout most of the runs 500 grams of prepared stock and 800 grams of water were used. On the water-free basis this became 98.85 grams of dry stock and 1201.15 grams of water, or practically 100 to 1200. This ratio was selected as the result of a few preliminary experiments. Ratios of 100 : 1400 and 100 : 1000 were tried. The results of these preliminary runs indicated that increases in the water ratio hastened somewhat the hydrolysis of collagen to gelatin, and retarded slightly or was without influence on the secondary hydrolysis of the gelatin to its degradation products. A decrease in the water ratio showed the opposite tendency.

From these observations it would appear that a high water ratio was desirable as it would produce the greatest amount of undegraded gelatin, but in the gelatin plant the optimum amount of water to use would be limited by the necessity later of evaporating off the excess, and in the present experiments it was desired to obtain a test for jelly consistency, and this would not have been feasible with the 100 : 1400 ratio. The 100 : 1200 ratio was very satisfactory from this point of view, while the 100 : 1000 runs showed a smaller recovery of nitrogen in the solutions, and a slightly greater secondary hydrolysis. The 100 : 1200 ratio was, therefore, adopted for this investigation.

EFFECT OF AGITATION

A few tests were made to determine the effect which agitation would produce on the hydrolysis. This was accomplished by blowing air through the hydrolyzing mixture. The air was first passed through potassium hydroxide, then through water at 80° C., and then into the stock solutions. Four different rates of flow were used, designated as rapid, medium, slow, and zero. The rapid was about ten bubbles per second; the medium, about four; and the slow, about one.

The results indicate that a rapid agitation hastens the primary hydrolysis of collagen to gelatin, but is without influence on the degradation of the gelatin. A rate of about two bubbles per second was employed throughout most of the experiments in this investigation.

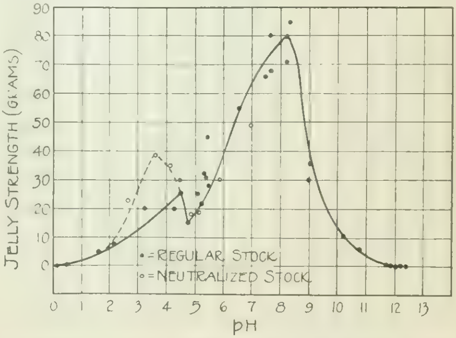

FIG. 5 EFFECT OF H-ION CONCENTRATION OF HYDROLYZING SOLUTION ON JELLY STRENGTH OF PRODUCT AT 10° C.

EFFECT OF CONDITION OF STOCK

A casual inspection of any lot of hide stock for manufacture into glue will show that it is of very un-uniform material.

Some of the pieces will be very thick and firm, others thin and limp. There will be a heavy layer of porous fatty material on the flesh side of some pieces and none on others. Some pieces will be covered with hair and other pieces will be entirely free of hair. The moisture content of these several types will also vary greatly. It is obvious, therefore, that very careful selection must be made if results of fair uniformity are to be obtained.

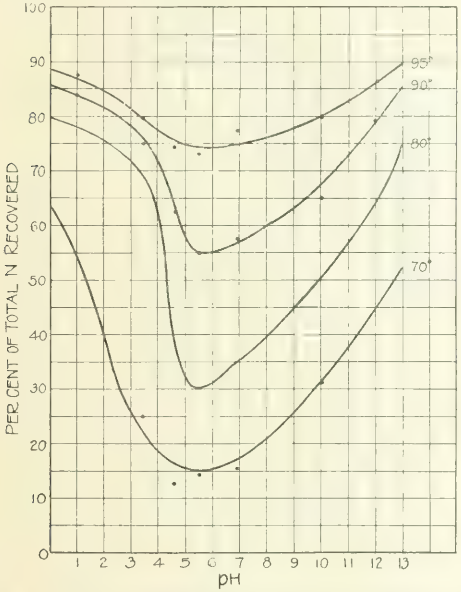

Fig. 6—Influence of Temperature on Total N Recovered in the Solution at Varying pH

The size to which the pieces were cut for the hydrolysis was found to influence greatly the rate of the reaction. Runs were made using large, thick pieces; strips about 2 inches long by $^1/_2$ inch in width and thickness; and pieces cut to approximately $^1/_4$-inch cubes. The recovery of nitrogen in the solution was much more rapid with the more finely cut pieces, and the secondary hydrolysis was also greater owing to the longer exposure of the gelatin produced. This latter degradation could be averted largely, however, by employing a shorter period of heating. It would seem that this should be of importance in the manufacturing processes, for by cutting the stock into very small pieces the hydrolysis of collagen to gelatin is accelerated, a shorter period of heating is required, and there will then be less opportunity for the gelatin to become further degraded. A larger yield of higher grade product should result.

The Plumping Reagent

The rate with which the collagen passes into solution is dependent in large measure upon the treatment which it has received prior to the hydrolysis. As a result of a series of swelling experiments, five reagents were selected as of especial merit, and the hide pieces swollen in them were subjected to hydrolysis and several tests made on the resulting solutions. The results are tabulated in Table I.

The water content of the dry, salted stock before treatment of any kind was 34 per cent. After thoroughly washing, during which process the salt, dirt, hair, etc., were removed (amounting to 33 per cent of the dry matter of the stock), the stock contained 70 per cent of water. As will be seen from the table, the water content was raised from 70 to 89 per cent in the lime solution, to 86 per cent in the lactic acid solution, and to lesser amounts in the others. But although the water content of the lime and lactic acid-swollen stock was about the same, their physical conditions were quite different. The former was firm and showed what might be called turgor. The latter was very limp and water could be easily squeezed out of it.

The lime-soaked stock gave the highest yield of nitrogen in the solution, and a moderate amino acid content. The highest viscosity and swelling were obtained with the borax, and the lowest amino acid content with the lactic acid. These irregularities may be in part due to the fact that equal weights of the swollen stock were employed in the hydrolysis rather than weights which would be equivalent on the dry basis. In general, however, the alkaline swelling reagents yielded a product that was firm and went most easily into solution, but the excessive hydrolysis into amino acids was more pronounced than in the acid-swollen stock. The latter was limp but gave solutions of good viscosity and jelly consistency.

General Discussion

The experiments described in this report have shown that many conditions affect the hydrolysis of collagen to gelatin. Of these, the hydrogen-ion concentration of the hydrolyzing solution, the temperature, and the duration of heating are apparently of greatest importance. All the curves recorded have been plotted against pH, and in all cases a minimum is observed in the region of the isoelectric point (between pH 4.5 and 5.5), and in every case, except the curve for ammonia evolved, the curves rise more or less rapidly on either the acid or alkaline side of that point. In the case of the ammonia evolved during the hydrolysis, the curve rises rapidly upon increasing concentrations of alkali, but remains uniformly low (practically negligible) at pH values less than 5.0.

The nitrogen recovered in the solution rises very rapidly on the acid side of the isoelectric point, increasing from about 30 per cent at pH 5.0 to about 7.0 per cent at pH 3.5. On the alkaline side the change is less rapid. The amino nitrogen of the solution remains low over a much greater range of pH, but above pH 9.0 this form of hydrolysis increases very rapidly.

The viscosity and jelly strength curves are nearly parallel and show two maxima, one on the acid and the other on the

Table I—Effect of Plumping Reagent on Hydrolysis

Reagent	$Ca(OH)_2$		$MgCO_3+NaOH$		Lactic Acid		Borax		Boric Acid	
Concentration, per cent	5		5 + 0.2		1		5		5	
Stock:										
Water	89.0		78.1		86.0		80.0		77.5	
Total nitrogen	14.09		14.21		14.13		14.00		14.08	
Solution:	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
Volume	1200	1200	1200	1250	1050	1050	1000	1000	1000	1000
Nitrogen in solution	82.4	82.3	76.4	77.2	70.6	67.1	78.8	74.6	71.3	72.5
Amino nitrogen	5.4	5.4	8.2	8.3	3.8	3.6	5.1	4.8	3.9	4.0
Nitrogen residue	17.6	17.7	23.6	22.8	29.4	32.9	21.2	25.4	28.7	27.5
Viscosity	85	86	115	107	146	126	128	135	105	114
Jelly strength	Liquid	Liquid	25	21	22	18	25	29	20	24
pH	9.2	9.2	8.8	9.0	4.2	4.2	7.9	7.9	4.9	5.0

alkaline side. The depressing effect due to the presence of salts (of calcium) in solution is shown especially well by these curves, for on the acid side much higher maxima come at about pH 3.5 and 8.0.

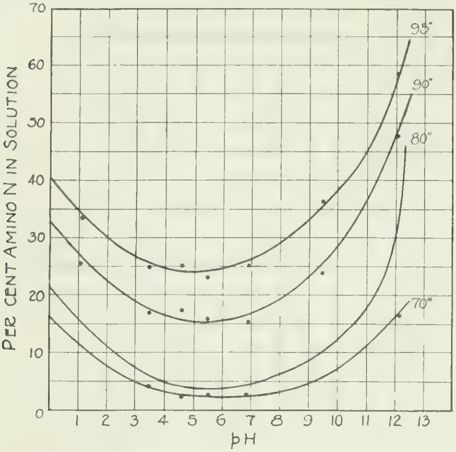

Fig. 7—Effect of Temperature on Amino N in the Solution at Varying pH

An increased temperature and a lengthened period of heating produce, throughout the entire range of pH, an increased hydrolysis both of collagen to gelatin (as shown by the nitrogen recovered in the solution) and of gelatin to its degradation products (as shown by the amino nitrogen of the solution). At very long periods of hydrolysis (168 hours), however, there appears on the alkaline side a drop in the nitrogen recovered in the solution. This is very probably due to the increased loss of nitrogen as ammonia under these conditions.

Theoretically, the most favorable results will be produced by a high ratio of water to stock, for, the concentration being less, it is shown that more of the stock will go into solution during a given period, and this will be degraded to a lesser extent than if concentrated, but, practically, a limit is set to the optimum dilution by the necessity later of evaporating the water off again to produce a liquid that will gel when cooled.

Agitation is also shown to hasten the hydrolysis, probably by keeping the concentration of the solution that is in direct contact with the stock as low as possible by disseminating the freshly dissolved material through the mass. The degradation to lower products is also increased slightly by agitation.

Very small pieces of stock were found to be dissolved with much greater rapidity than large pieces. The secondary hydrolysis was also increased, but it seems probable that a shorter period of heating or a lower temperature could advantageously be utilized with finely cut material.

Alkaline plumping or swelling reagents were found to yield a stock that was firmer than acid-plumped stock, and that dissolved somewhat more rapidly, but a larger amount of the solution was degraded. Acid-plumped stock was limp, but gave a product of good viscosity and jelly consistency.

There was no evidence obtained which would indicate that ammonia was evolved upon the hydrolysis only of collagen to gelatin. That ammonia was evolved upon the alkaline hydrolysis of collagen was demonstrated, but from the examination of the curves showing the amino nitrogen production upon the same treatment, it appears that the ammonia nitrogen formation may be adequately accounted for as being due to a more complete breakdown of the molecule. Amino nitrogen can be increased only by hydrolytic scission of the large molecules. The formation of proteoses or peptones,

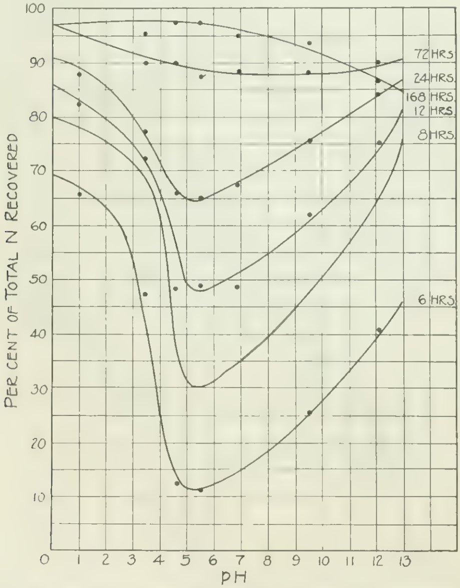

Fig. 8—Effect of Period of Heating on Total N Recovered in the Solution at Varying pH

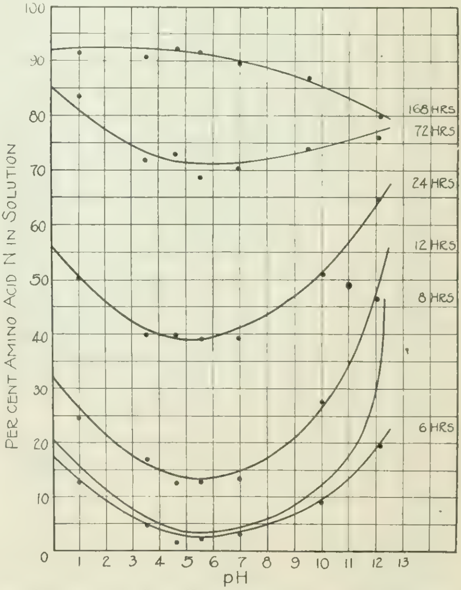

Fig. 9—Effect of Period of Heating on Amino N in Solution at Varying pH

as well as of free amino acids, increases the amino nitrogen determinable. That this same operation produces also ammonia has been shown in the hydrolysis of gelatin by Fischer,[10] Daken,[11] Van Slyke,[12] Bogue,[13] and others. It seems probable to the writer that collagen is a polymerized complex of gelatin. Upon heating gelatin to 130° C. an anhydride is probably produced, but this is not similar to the original collagen. The polymerization seems to be chemical rather than physical, and would, therefore, be comparable to the relation between gelatin and proteose, or between proteose and peptone. Neither of the latter can be treated to reproduce gelatin, and it seems very doubtful if gelatin can be treated so as to reproduce collagen.

The optimum conditions for hydrolysis of collagen to gelatin are, of course, those by which the greatest amount of nitrogen passes into solution in the shortest period of time, but during which process the minimum amount of degradation of the gelatin takes place. In the experiment reported, these conditions seem to be best attained by the following control:

1—The hydrogen-ion concentration of the hydrolyzing solution should be such that the resulting gelatin or glue solution will possess an H-ion concentration between pH 3.0 and 4.0 or between pH 7.5 and 8.5. The region of pH 4.5 to 6.0 should be avoided as the hydrolysis is very slow at that concentration of hydrogen ions. Above pH 8.5 the degradation of the gelatin becomes too great, with a corresponding loss of nitrogen as ammonia, and below pH 3.0 there is also a degradation, while in both cases the velocity and jelly strength of the product become very low.

2—A temperature of 80° C. seems most favorable to the hydrolysis of collagen to gelatin, and an 8-hour period of heating is satisfactory. There is too little hydrolysis at lower temperatures or shorter periods of heating (although a somewhat purer product may result under these conditions), while at higher temperatures and longer periods the greatly increased degradation of the gelatin offsets any advantages of more rapid collagen hydrolysis.

3—The optimum ratio of dry stock to hydrolyzing solution (including water in the stock) seems to be about 1:12 or 1:14. Lower concentrations necessitate later evaporation, while greater concentrations give lower yields of gelatin and increased degradation of the gelatin formed.

4—The stock may be swollen in a number of different reagents, lime and lactic acid showing the best results to date, but the excess of reagent should be removed completely by washing and neutralization, as a depressing effect on the viscosity and jelly strength may result from their presence.

5—A fine cutting of the stock and constant agitation are desirable as they make possible a more rapid hydrolysis, but to prevent also a more rapid degradation of the gelatin a shorter period of heating or a lower temperature will be necessary. A 6 or 7-hour heating at a temperature of 75° C. probably will produce, with finely cut stock and thorough agitation, about the same hydrolysis as an 8-hour heating at 80° C. under the opposite conditions.

Acknowledgment

The writer wishes to express his indebtedness to C. K. M. Ritchie for performing a number of the determinations reported herein.

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[10] Fischer, Levene, and Anders, *Z. Physiol. Chem.*, **35**, 70 (1902).

[11] *J. Biol. Chem.*, **44**, 524 (1920).

[12] *Ibid.*, **10**, 48 (1911).

[13] *Chem. Met. Eng.*, **23**, 156 (1920)

Extraction and Recovery of Radium, Vanadium, and Uranium from Carnotite[1]

By K. B. Thews and F. J. Heinle

Keystone Metals Reduction Co., Cheswick, Pa.

The carnotite ores now mined in Colorado and Utah are of too low a quality to permit handling and shipping to the reduction plants without first picking out the higher grade ores or else concentrating this ore. The practice in almost all cases is to pick out the higher grade material, which makes it necessary to store in the field large quantities of low-grade carnotite, and it appears that in the future American radium manufacturers will be forced to concentrate all these ores before shipment to the plants is profitable. For this reason, the writers have described in detail the extraction of the values from concentrates instead of ores, and have only mentioned the advantages occurring in extracting the values from ores.

Radium Extraction and Recovery

In iron tanks or pressure boiling kettles the following mixture is made—2 parts water, 1 part concentrates, and approximately 200 pounds of soda ash for each per cent of uranium oxide present. This mixed mass is boiled with continuous stirring for from 6 to 10 hours. Should this boiling be done in an open tank and coils used for heating, a small amount of the condensed steam should be returned into the boiling tank to take care of the evaporation of the water. Otherwise, the mass would boil down to the concentration point of soda salts, which would result in the crystallizing out of the uranium salts as the sodium uranyl carbonate. A more complete conversion is made in pressure kettles because of greater heat, and practically all companies using this process have installed pressure kettles.

The object of this carbonation is to convert the acid-insoluble barium and radium salts to the acid-soluble barium and radium carbonates, also to convert about 90 per cent of the uranium to the soluble sodium uranyl carbonate and some of the vanadium to the soluble sodium vanadate.

It has been found that in a concentrate about 90 per cent of the uranium and about 30 per cent of the vanadium are converted to soluble salts. This carbonation should be made in three series, each large enough to supply the plant with a full day's run. In this manner the concentrate is boiled one day, settled the second, and decanted and filter-pressed on the third day. After decantation the mass is pumped into a washing type, iron filter press and the cake washed with sulfate-free water until the resulting filtrate is free from sulfate. From 6 to 10 hours are required to accomplish this washing. All the decanted liquor, filtrate from press, and part of the wash water containing the soluble vanadium and uranium salts are pumped into evaporating tanks (recovery later), and the remaining wash water is used as mix for new conversions. The cake in the filter press containing the radium is carefully taken out, broken up with about 20 per cent of sulfate-free water in a paddle tank, and pumped into the acid-treating tanks. These tanks resist the action of the acid and are so constructed that the mass can be stirred well. Enough sulfate-free hydrochloric acid is added to neutralize all carbonates, etc., and to acidify the solution. A solution of 2 per cent

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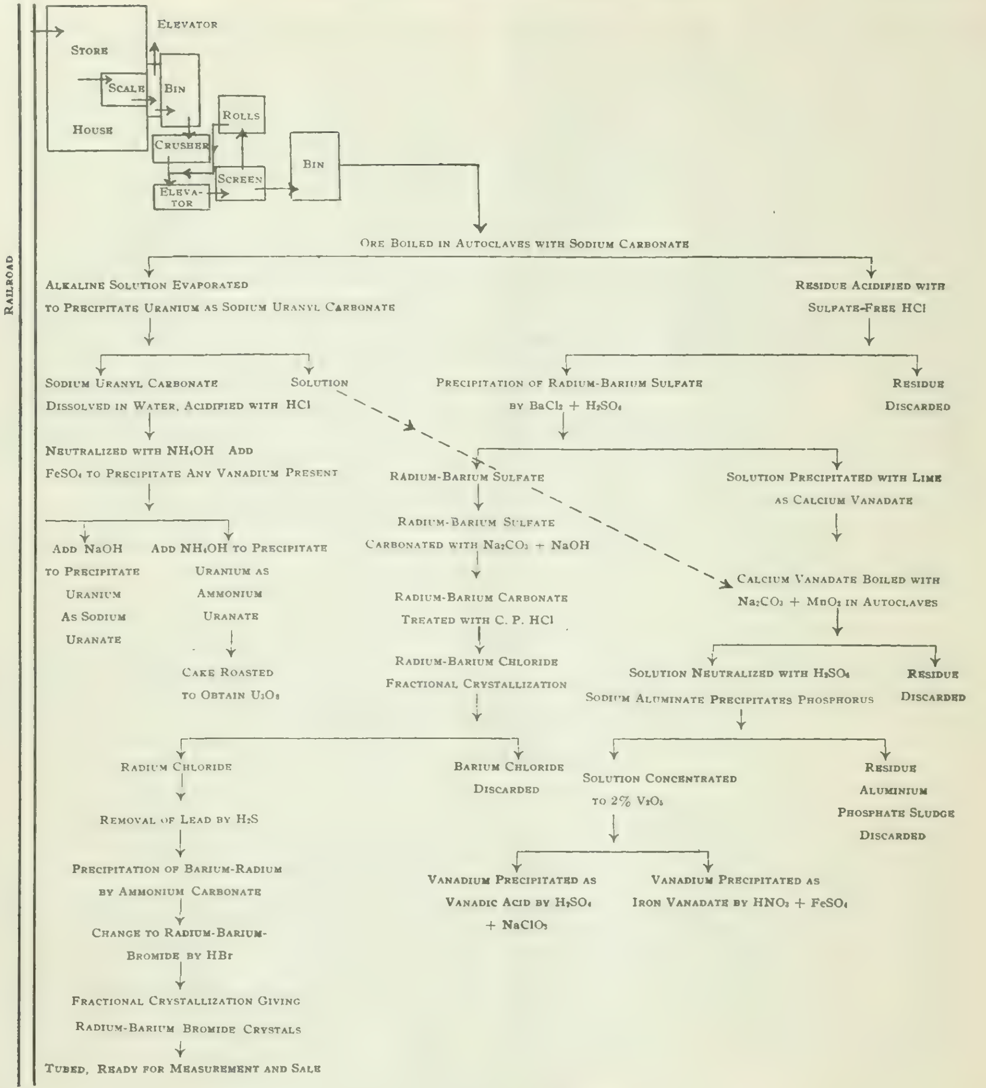
[1] Received June 28, 1923.


Railroad
Store
House
Scale
Elevator
Bin
Rolls
Crusher
Screen
Elevator
Bin
Ore Boiled in Autoclaves with Sodium Carbonate
Alkaline Solution Evaporated to Precipitate Uranium as Sodium Uranyl Carbonate
Residue Acidified with Sulfate-Free HCl
Sodium Uranyl Carbonate Dissolved in Water, Acidified with HCl
Solution
Precipitation of Radium-Barium Sulfate by $BaCl_2 + H_2SO_4$
Residue Discarded
Neutralized with NH_4OH Add $FeSO_4$ to Precipitate Any Vanadium Present
Radium-Barium Sulfate
Solution Precipitated with Lime as Calcium Vanadate
Add NaOH to Precipitate Uranium As Sodium Uranate
Add NH_4OH to Precipitate Uranium as Ammonium Uranate
Radium-Barium Sulfate Carbonated with Na_2CO_3 + NaOH
Calcium Vanadate Boiled with $Na_2CO_3 + MnO_2$ in Autoclaves
Radium-Barium Carbonate Treated with C. P. HCl
Cake Roasted to Obtain U_3O_8
Radium-Barium Chloride Fractional Crystallization
Solution Neutralized with H_2SO_4 Sodium Aluminate Precipitates Phosphorus
Residue Discarded
Radium Chloride
Barium Chloride Discarded
Solution Concentrated to 2% V_2O_5
Residue Aluminium Phosphate Sludge Discarded
Removal of Lead by H_2S
Precipitation of Barium-Radium by Ammonium Carbonate
Vanadium Precipitated as Vanadic Acid by H_2SO_4 + $NaClO_3$
Vanadium Precipitated as Iron Vanadate by $HNO_3 + FeSO_4$
Change to Radium-Barium-Bromide by HBr
Fractional Crystallization Giving Radium-Barium Bromide Crystals
Tubed, Ready for Measurement and Sale

Flow Sheet of Radium Process

acidity is generally sufficient for this purpose. The acid-consuming number can be easily found by taking a 100-gram sample of the carbonated cake, acidifying, and boiling it with a given quantity of hydrochloric acid and then titrating the filtrate with a normal caustic solution. The excess needed can then easily be calculated. The acidified mass, in tanks, is then boiled for 20 to 60 minutes and pushed into washing-type, wooden filter presses, by means of a blow case, and washed with sulfate-free water until the resulting wash waters are barium-free. The filtrate and wash waters will now contain over 90 per cent of the radium and about 80 per cent of the vanadium not taken out by the carbonate conversion. The cake in the filter press is free from radium, vanadium, and uranium and can be discarded. The filtrate wash waters are run into large boiling tanks and the radium is precipitated with sulfuric acid, or a soluble sulfate, such as sodium acid sulfate. In case no barium has been introduced, a small quantity (about one-half pound) of barium chloride per milligram of radium present is added before this precipitation is made. The precipitated radium barium sulfates are left to settle for from 2 to 4 days, when most of the liquor containing the vanadium is decanted off, and the remaining liquor plus the precipitated sulfates dropped on vacuum filters and the liquor separated from the cake. This radium barium sulfate will contain about 1200 milligrams per ton; therefore, a concentration of 1 to 100 or more has been made.

The cake containing all the radium and barium as sulfates is washed and mixed in an autoclave with two parts of its dry weight of soda ash, 10 per cent caustic soda, and four parts of water, and boiled for about 12 hours. The radium barium carbonates resulting from this conversion plus liquors are pumped into a small, washing type, iron filter press, and washed sulfate-free with distilled water. The cake containing the radium and barium is taken out carefully and treated with C. P. hydrochloric acid. After filtering, the radium in the filtrate is ready for fractional crystallization. This is done by either the neutral or acid method of crystallization. Since many publications have been written on the fractional crystallization of radium, the writers will not describe it in this paper.

Plant Control of Radium

Chemical plant control is a very important factor and is carried out with great care. Possible contaminations by sulfates must be guarded against and eliminated, and since the ore contains sulfates and sulfuric acid is used in the process, contaminations are easily possible. Rapid qualitative tests for sulfates are made repeatedly, especially after the carbonate conversions and before the hydrochloric acid treatment. The hydrochloric acid treatment department is generally kept away from the other departments for this reason, and all operators are warned to keep clothing such as shoes, etc., in clean condition. At this point sulfates will do most of the damage. Should sulfates enter, reprecipitate some of the radium to insoluble sulfate, a costly reconversion with sodium carbonate is necessary.

Extraction from Ores

Most of the radium plants today do not concentrate their ores but resort to hand picking and shipping this picked ore to their plants. In this case the ore is first crushed and ground to from 20 to 30-mesh before the values are converted with sodium carbonate, and after the first hydrochloric acid treatment the slimes and liquors are decanted off and pumped into filter presses. Since the average ore, after crushing, consists of about 15 per cent of slimes and 85 per cent sandy material, and since the sands after acid treatment contain practically no radium, this decantation results in a considerable saving in labor and equipment. A few washes after the main liquor has been decanted off will free the sands from all values. Otherwise, ores are treated the same as concentrates.

Uranium Recovery

The liquor from the first carbonation, containing about 90 per cent of the uranium and some of the vanadium, is pumped into large tanks and evaporated until the concentration point of the contained soda ash is reached. This point can be ascertained by blowing a film on the top of a sample taken from the solution. At this point all the uranium crystallizes out as the sodium uranyl carbonate, and the vanadium remains in the liquor. The mass is filtered and the sodium uranyl carbonate slightly washed with cold water. The sodium uranyl carbonate is dumped into a wooden tank and enough water added to dissolve the salt. The mixture is then slightly acidified and boiled to drive off all carbonates and almost neutralized with ammonia. A little vanadium is carried along with the uranium, and for the purpose of eliminating this vanadium a small quantity of ferrous sulfate is added. After the iron vanadate has been separated from this solution by filtration, the uranium is precipitated with ammonium hydroxide as the ammonium uranate. The precipitated mass is pumped into a washing type, iron filter press and the cake washed until all the soda salts have been removed. The ammonium uranate is put into a roasting furnace and converted to the uranium oxide by heat. A small amount of the uranium will be precipitated as sodium salts, owing to the soda salts present, but it has been found that an oxide of 97 per cent purity can be made. In case a purer salt is wanted the ammonium uranate is redissolved and reprecipitated.

If caustic soda is used after the solution has been freed from the vanadium, sodium uranate is precipitated.

Vanadium Recovery

The vanadium in the acid solution decanted from the precipitated barium radium sulfate is pumped into large stirring tanks, boiled, and the vanadium precipitated with lime as the calcium vanadate, filtered, and washed. The cake containing the vanadium is then mixed with the liquor from the sodium uranyl carbonate evaporation plus 10 per cent of sodium carbonate, a small amount of oxidizing agent such as manganese dioxide, and boiled for 2 hours. By adding the liquor from the sodium uranyl carbonate evaporation to the lime cake, vanadium is not only combined, but a considerable saving in soda ash is made. The boiled mass is pumped into washing type, iron presses and the cake washed free of vanadium. About 95 to 98 per cent of the vanadium is now in solution. The cake can be discarded. This solution is pumped into wooden tanks, almost neutralized with sulfuric acid, and the phosphorus from the ore carried along, precipitated with sodium aluminate as an aluminium phosphate sludge. This sludge is filtered off and the solution is pumped into an evaporating tank and boiled until a 2 per cent vanadium solution is reached. This is then precipitated as the vanadic acid by adding a slight excess of sulfuric acid and boiling vigorously. It has been found that sulfuric acid will not precipitate vanadium in weak solution and that when a solution is concentrated to about 2 per cent V_2O_5 content, the most efficient results are obtained. A vanadic acid containing 80 per cent V_2O_5 can be precipitated by this method. This precipitated vanadic acid is filter-pressed, washed free from sulfates, and dried. The resulting vanadium oxide is ready for reduction. In case iron vanadate is wanted, the solution does not have to be evaporated, but is almost acidified with sulfuric acid, and after dephosphorization slightly acidified with nitric acid and the vanadium precipitated with ferrous sulfate. By decreasing or increasing the excess acidity, iron vanadate of various purities can be made. A higher acidity will give a higher grade concentrate.

Conclusion

The process described has its disadvantages when compared with others such as the nitric acid,[2] sulfuric acid leaching,[3] niter cake fusion[4] processes. It requires more equipment, more careful checking, and the solutions and cakes have to be handled more frequently. Its chief advantage lies in the fact that when operated carefully, purer and more easily worked solutions result. Under normal conditions, recoveries of 80 per cent or better of all values in carnotite are being made. There is very little difference in costs of operation between these processes, so this process is today the most popular one used on carnotite ores.

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[2] Parsons, Moore, Lind, and Schaefer, *Bur. Mines, Bull.* **104.**

[3] Fleck, Haldane, and White, U. S. Patent 890,584.

[4] Schlundt, U. S. Patent (?).

Indiana Section Aids Fire Department

At the request of the chief of the fire prevention division of the Indianapolis Fire Department a committee headed by Cecil Calvert will prepare instructions for the use of firemen when handling fires in which acids or other chemicals that might cause explosions or spread dangerous gases are encountered. The recent unfortunate experience of the Milwaukee department led to the request and the organization of the committee. Possibly other sections may find that they can similarly serve their own communities.

The Biological and Chemical Significance of Gamma Sugars[1]

By James Colquhoun Irvine

United College of St Salvator and St. Leonard, The University, St Andrews, Scotland

This article is a brief review of the present knowledge of gamma sugars. The name is applied to all forms of sugars in which the oxygen ring is displaced from the normal, stable position. The discovery of these sugars was the result of gradually accumulated evidence beginning from work by the author on the methylation of sucrose and the separation of the sugars formed on hydrolysis, when it was found that the methylated fructose was dextrorotatory.

The reactions show properties entirely different from those of normal sugars. Experiment points to the theory that the natural processes leading to formation of sugars involve the formation of gamma sugars as intermediate stages. It is possible that these are not chemical individuals, but only a condition of the sugar molecule.

NO ATTEMPT has hitherto been made to compile a general survey of our knowledge regarding the reactive types of reducing carbon hydrates which are known collectively as gamma sugars. Although these important variations of sugar molecules have been recognized for some years, they present unusual difficulties to penetrative study, and despite laborious research still remain largely obscure and unexplained. Nevertheless, they have recently been invested with a special interest and are referred to with a freedom which displays the necessity to review what is known regarding them.

Reason for Name

To begin with, the name applied to them is not descriptive, but is, in a sense, accidental. As is well known, the best-defined reducing sugars can generally be obtained in two isomeric forms which display mutarotation in opposite directions, and this is attributed to the rearrangement of the groups in the reducing position. The expressions "alpha" and "beta" were applied to designate these isomerides, and the two mutarotatory forms of glucose serve as standard examples in illustration. Now this isomerism has been proved to be in no way dependent on the position of the internal oxygen ring in the sugar, since both α- and β-glucose have been correlated with the butylene oxide form of tetramethylglucose. The discovery that another variety of glucose exists, in which the oxygen ring is differently attached, could not be accommodated by the nomenclature then in use and the expression "γ-glucose" was applied to it. The name "gamma sugar" has therefore a very general significance and is used to include all forms in which the oxygen ring is displaced from the normal stable position. This is not entirely satisfactory, but a more exact nomenclature cannot be applied until the complete structure of each of these sugars has been established. Meanwhile, it may prevent confusion if it is pointed out that gamma sugars, retaining as they do a reducing group, can exist in alpha and beta modifications, and the same remark applies to their glucosides.

Up to the present it has been ascertained that glucose, galactose, mannose, rhamnose, and fructose are all capable of existing in gamma forms, and there seems no reason to doubt that the property is general. In no case, however, has an unsubstituted gamma sugar been isolated, although we recognize their transient existence, and can in some measure study their properties by examining their methylated derivatives. The presence of the methyl groups in these derivatives prevents any alteration in the oxygen ring, and thus the constitutional type is preserved.

Discovery

Before summarizing the chemistry of gamma sugars, it may be mentioned that their discovery did not originate in any single dramatic observation, but that the evidence accumulated gradually. One of the writer's laboratory notebooks, describing work carried out exactly twenty years ago, gives an account of the methylation of sucrose, and the separation of the sugars thereafter formed on hydrolysis. Crystalline tetramethylglucose was isolated and, in addition, the corresponding fructose derivative was obtained by means of condensation with methanol at room temperature, followed by the usual fractional distillation and hydrolysis. The complete analysis of the product was carried out, its composition was ascertained to be that of a tetramethylfructose, and its specific rotation was shown to be of the order +27°. The entry in the book states that the work was at this stage suspended, there being no adequate explanation as to why a methylated fructose should be dextrorotatory. The compound was, in fact, pure tetramethyl-γ-fructose, but many consecutive researches were necessary before the discovery could be interpreted. A subsequent paper on the methylation of fructose added materially to the evidence that the ketose can react in a dextrorotatory form, and about the same time a result of equal significance was forthcoming. A levorotatory trimethylglucose was obtained from glucosemonoacetone, and in investigating the origin of this compound a new levorotatory form of tetramethylmethylglucoside was isolated, *thus showing that not only can d-fructose react in a dextro form, but d-glucose can exist in a levorotatory variety.*

At this stage Fischer published his paper on γ-methylglucoside, which was quickly followed by our account of the isolation and properties of tetramethyl-γ-glucose. In view of this theoretical development, the way was now clear to resume the study of sucrose and to expand the scope of the work.

Properties

For reasons already stated, the properties of gamma sugars have to be inferred from those of their methylated derivatives and, so far, the following examples, together with the corresponding methylglucosides, are available for study:

Tetramethyl-γ-glucose (levo)
Trimethyl-γ-glucose (levo)
Tetramethyl-γ-galactose (levo)
Tetramethyl-γ-mannose (levo)
Tetramethyl-γ-fructose (dextro)
Trimethyl-γ-fructose (dextro)

In reviewing their reactions, one is struck by the close resemblance shown to natural processes. For example, the compounds undergo oxidation with extreme ease, being affected by mild oxidizing agents, and in illustration it may be mentioned that trimethyl-γ-glucose reduces Fehling's solution instantaneously at room temperature. At ordinary temperatures, also, they are converted into glucosides, at a speed which is remarkable, especially when it is remembered that the formation of α-methylglucoside requires a treatment of approximately 60 hours at 100° C. In at least one case (tetramethyl-γ-galactose), a reducing sugar of the gamma type is known to pass spontaneously by autocondensation into a nonreducing disaccharide. These striking properties are far removed from those of a normal sugar.

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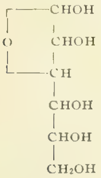
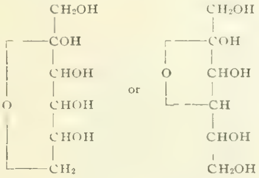
[1] Presented before the Division of Sugar Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

Constitution

Great difficulties have been encountered in attempts to solve the constitution of gamma sugars, and experimental work has been largely confined to tetramethyl-γ-glucose, trimethyl-γ-fructose, and tetramethyl-γ-fructose. In the case of the glucose derivative, the first opinion formed was that an ethylene oxide ring was present, but this view has been modified in favor of the propylene oxide structure. Similarly, an amylene oxide constitution is at present supported for tetramethyl-γ-fructose, so that meanwhile the parent sugars may be represented as:



γ-Glucose



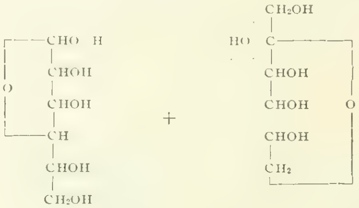
γ-Fructose

It is already evident that the butylene oxide structure cannot be assumed for any sugar, even in its most stable form. Thus, crystalline xylose, which displays none of the properties of a gamma sugar, has recently been shown to be an amylene oxide, and in this respect at least resembles γ-fructose.

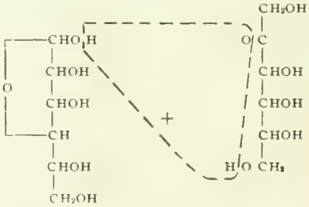
Speculation in the absence of experiment is best avoided in the carbohydrates, but in the course of investigating many varieties of gamma compounds, it was found impossible to reject the idea that the ordinary, crystalline, comparatively stable sugars of the laboratory are not the forms which are primarily elaborated by the plant or disrupted by the animal. The fructose which we store in the chemical museum, and produce as a lecture specimen, is not fructose as it exists in combination in sucrose or in inulin.

The idea conveyed above is that the natural processes leading to the formation of sugars and their derivatives, as also the ultimate utilization of carbohydrates by the animal organism, involve as intermediate stages the transient formation of gamma sugars. The evidence may not be particularly convincing save to those who have handled all types of carbohydrates at the working bench, but it is certainly true that we have fleeting glimpses of extraordinarily reactive sugars which in the process of artificial isolation from either plant or animal sources undergo rearrangement to the sugars as we know them. This is not inconsistent with the results obtained in either hydrolysis or synthesis effected by enzymes. If this suggestion is substantiated, it may have far-reaching effects in studying physiological processes, and in the treatment of conditions such as diabetes in which the metabolism of sugars is abnormal. Research designed to test this idea was commenced three years ago, and the first tentative steps have been taken to ascertain if living tissue promotes the formation of γ-glucose. The evidence obtained is encouraging, but further progress is hampered by the inaccessibility of gamma sugars, and the lack of trustworthy methods of identifying them. When it is remembered that γ-glucose and γ-fructose revert instantaneously to their respective stable forms in the presence of 0.1 per cent of hydrochloric acid, it will be agreed that there is little prospect of detecting these fugitive isomerides by ordinary processes. Analytical methods are of no avail, and polarimetric evidence alone is insufficient and often misleading. No doubt these difficulties will be surmounted in time, but only when the detailed chemistry of gamma sugars has been advanced on systematic lines, and when knowledge exceeds impatience.

Having in a sense created gamma sugars for you, it may appear contradictory to say that it is doubtful whether these substances are, after all, chemical individuals. They may only represent a condition of the sugar molecule which originates in the mechanism whereby a sugar forms certain of its derivatives. To make the point clear by means of an example, we need not assume that in the formation of sucrose a molecule of normal glucose condenses with a molecule of γ-fructose in such a manner that each loses a hydroxyl group:



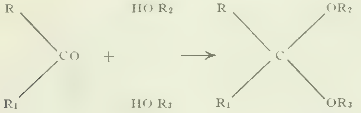
It is possible that γ-fructose may have no real existence, and the condensation may be equally well explained on the assumption that fructose functions as a ketone. In such a case, two hydroxyl groups become involved, and although one of these must be the reducing group of the aldose molecule, there is no reason, once the reaction is initiated, why the ketose itself should not furnish the second group:



An amylene oxide ring is thus formed in the ketose component and here we see *the production of a gamma residue without the previous existence of a gamma sugar.* Similar considerations apply to the formation of γ-glucose derivatives which may be formed in condensation reactions in which glucose reacts as an aldehyde. These suggestions are not without the support afforded by numerous analyses, and meanwhile the whole subject is a maze of possibilities, and enlightenment is still remote.

For example, if the question is raised as to why sucrose is so remarkably unstable towards hydrolysis, the existence of an amylene oxide ring in the fructose component provides no answer. Methyl xyloside is likewise an amylene oxide; yet the compound resists the effect of dilute acids, while β-glucosan, which contains a hexylene oxide ring, is notably stable. Again, fructose mono- and di-acetones both undergo hydrolysis with a facility which resembles that displayed by sucrose, but nevertheless both of these compounds are based on the stable type of fructose in which a butylene oxide ring is present. These apparently contradictory results reveal that the special instability of gamma derivatives does not depend primarily on the presence of any particular internal ring in the sugar.

On the other hand, when aldehydes or ketones condense with hydroxy compounds (including sugars), the products resemble sucrose in their ease of hydrolysis. Numerous isopropylidene and benzylidene derivatives may be quoted in illustration, and the reactions in which such compounds are formed have been shown to follow the course indicated below:



Applying this to the special case of carbohydrates, gamma sugars may be regarded in a new light—γ-fructose may, in fact, be nothing more than the ketonic form of the sugar, and γ-glucose the corresponding aldehyde. It may well be that the aldoses and ketoses functioning in their primary capacity as aldehyde and ketone are the reactive sugars in nature, but this much seems clear—no naturally occurring compound of glucose, whether glucoside, disaccharide or polysaccharide, has been found to contain the γ-glucose structure, and the reactive type of the sugar has hitherto been obtained only under artificial conditions. In sharp contrast, the two most important natural derivatives of fructose are each based on γ-fructose, which may possibly prove to be the connecting link in natural processes whereby the interconversion of ketoses and aldoses is effected.

Effect of Acids and Salts upon the Hydrolysis of Wood[1]

By **E. C. Sherrard and W. H. Gauger**

Forest Products Laboratory, Madison, Wis.

The effect of several salts upon the acid hydrolysis of wood is described, as well as the effect of several acids, when used alone and in conjunction with mineral acids. A study was made regarding the quantity of sugar produced from white spruce by varying the concentration of sulfuric acid from 5 to 30 per cent. The effect of time and pressure upon sugar yields is also described. The effect of temperature upon mannose indicates that its rate of decomposition under similar conditions is practically the same as that of glucose.

In a previous paper[2] it was pointed out that the use of salts in connection with a dilute mineral acid gave variable results, and that no close prediction could be drawn regarding the effect of these salts upon the quantity or nature of sugar produced. Since then the effect of a few additional salts has been studied, as well as the effect of several organic acids when used alone and in conjunction with a dilute mineral acid. The same procedure was used as previously described. Unless otherwise noted, the salt or acid was added to a mixture of 100 grams white spruce sawdust, 200 grams water, and 2.5 grams (100 per cent) sulfuric or hydrochloric acid, and the mixture subjected to a steam pressure of 115 pounds (175° C.) in an autoclave for 15 minutes. The blank experiment in which sulfuric acid was used alone gave a yield of 21.14 per cent of reducing sugar, of which 66 per cent was fermentable, or 21.35 gallons of 95 per cent ethyl alcohol per ton of dry wood.

The salts used in this case gave no great variation in yield, as will be noted in Table I.

Table I—Salts

Cook No.	Catalyst	Per cent Reducing Sugar in Terms of Dry Wood	Per cent Sugar Fermentable	Alcohol Gallons per Ton of Dry Wood	Remarks
74	1.25% $BaCl_2$ (HCl)	22.70	69.2	22.8	
78	0.5% $Al_2(SO_4)_3$	18.86	38.5	9.0	Fermented with difficulty
79	0.5% K_2SO_4	21.50	61.7	19.4	
80	0.5% $ZnCl_2$(HCl)	22.58	69.2	21.7	
81	1 25% $Ca(NO_3)_2$	21.74	67.3	21.0	

Here, as before, no outstanding increases in yields were obtained, although barium chloride and zinc chloride in the presence of hydrochloric acid gave yields slightly greater than were obtained in the blank experiment.

The yields of total reducing sugar and alcohol obtained by the use of different acids are given in Table II.

Of the acids studied the most promising are the naphthalene sulfonic acids, although it is of interest to note that oxalic acid gave a yield of sugar that compares favorably with those of stronger acids. Trichloracetic acid gave the poorest results of any of the acids tried.

Table II—Acids

Cook No.	Catalyst	Per cent Reducing Sugar in Terms of Dry Wood	Per cent Sugar Fermentable	Alcohol Gallons per Ton of Dry Wood
68	1.8% H_3PO_4 (alone)	16.66	49.00	11.4
69	2.5% H_3PO_4 (alone)	16.45	51.3	12.3
71	1.8% $Cl_3C—\overset{\diagup\!\diagup O}{C}—OH$ (alone)	3.75	No fermentation	
72	2.5% $Cl_3C\overset{\diagup\!\diagup O}{C}—OH$ (alone)	2.30	No fermentation	
73	2.5% $Cl_3C—\overset{\diagup\!\diagup O}{C}—OH$ (alone)	3.41	No fermentation	
75	0.5% H_3BO_3	22.59	63.5	20.5
76	1.7% $C_6H_5SO_3H$ (alone)	20.35	55.0	16.6
77	2.5% $C_6H_5SO_3H$ (alone)	22.68	56.0	17.4
82	0.5% $C_{10}H_6\begin{matrix}\diagup OH \\ \diagdown SO_3H\end{matrix}$	23.28	59.9	20.8
83	2.0% $C_{10}H_4\begin{matrix}\diagup (OH)_2 \\ \diagdown (SO_3H)_2\end{matrix}$	24.46	61.4	22.1
84	2.0% $C_{10}H_4\begin{matrix}\diagup (OH)_2 \\ \diagdown (SO_3H)_2\end{matrix}$ (alone)	11.14	28.7	4.9
85	1.95% $C_6H_5SO_3H$	23.76	60.3	20.1
86	5% $H\overset{\diagup\!\diagup O}{C}—OH$ (alone)	12.34	Not fermentable	
87	5% $\begin{matrix}\overset{\diagup\!\diagup O}{C}—OH \\ \vert \\ \underset{\diagdown\!\diagdown O}{C}—OH\end{matrix}$ (alone)	22.45	58.2	19.7
88	1.25% $C_6H_5\overset{\diagup\!\diagup (OH)_3}{} \overset{\diagup\!\diagup O}{C}\ OH$	22.82	60.0	20.9
89	0.5% $C_6H_4\overset{\diagup NH_2}{—}SO_3H$	23.01	63.2	22.1
90	1.25% $C_6H_4\overset{\diagup NH_2}{—}SO_3H$	22.88	62.5	21.8

Apparently, the acid decomposed under the condition imposed, for in every case where trichloracetic acid was used the odor of chloroform was noticed in the digested material.

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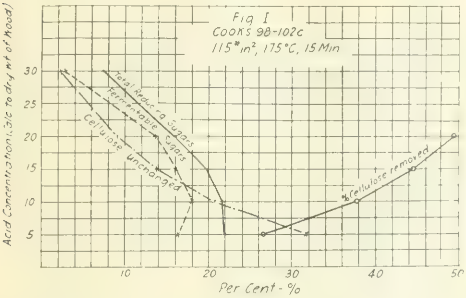
[1] Presented before the Division of Cellulose Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] This Journal, **15**, 63 (1923).

No effort was made, however, to identify it accurately. The yields obtained by the use of phosphoric acid were surprisingly low. Kressmann[8] reports a yield of sugar of 19.38 per cent and 15.66 gallons of 95 per cent alcohol per ton. Sulfanilic acid also gave yields somewhat higher than were obtained in the blank.



Kressmann studied the effect of sulfuric acid by varying the concentration up to 5 per cent. It was now decided to continue increasing the acid concentration until the fermentable sugars showed a decided decrease. To complete the study the residues from each cook were analyzed for cellulose by the Cross and Bevan method, in order to determine the extent to which decomposition occurs during the treatment. The concentration of sulfuric acid was varied between 5 and 30 per cent, with the results given in Table III.

TABLE III

Grams of H_2SO_4 per 100 of Dry Wood	Per cent of Original Dry Wood: Total Reducing Sugars	Fermentable Sugars	Cellulose Unchanged	Cellulose Removed
5	21.98	16.29	31.7	26.5
10	21.54	18.00	20.46	37.74
15	19.71	16.10	13.71	44.50
20	16.00	13.67	8.95	49.25
30	7.28	2.70	2.14	56.06

It will be noticed that after a maximum is reached a fairly uniform decrease of total reducing sugars and fermentable sugars occurs, while the cellulose removed increases very rapidly. Since the ratio of sugar to cellulose removed increases with the concentration of acid, it appears that the sugars are destroyed more rapidly than the cellulose is hydrolyzed. These changes are shown somewhat more clearly in Fig. I.

The yield of fermentable sugar having been materially increased by the use of 10 per cent sulfuric acid for 15 minutes, a second set of experiments was run in which the acid concentration was held constant at 10 per cent but the time factor was varied. Here again the yield of fermentable sugars passed through a maximum, although the subsequent drop was gradual. The maximum in this series of experiments came with an acid concentration of 10 per cent and a cook of 10 minutes' duration at 115 pounds' steam pressure (175° C.). The results may be seen in Table IV.

TABLE IV

Cook No.	Time Min.	Pressure Lbs./Sq In.	H_2SO_4 in Per cent of Dry Wood	Total Per cent Reducing Sugars	Per cent Sugars Fermentable	Alcohol Yield Per cent	Gallons Alcohol per Ton of Dry Wood
104c	5	115	10	21.54	13.50	6.88	20.80
105c	10	115	10	23.98	17.02	8.67	26.30
99c	15	115	10	21.54	16.54	8.45	25.60
108c	15	115	10	22.35	16.64	8.47	25.67
106c	20	115	10	21.42	15.85	8.10	24.55
109c	25	115	10	21.92	16.18	8.27	25.05

Having varied acid and time factors, the pressure factor was now studied, and a series of experiments was performed using 7.5 per cent sulfuric acid cooking for 15 minutes and varying the pressure from 80 pounds in Cook 110c to 125 pounds in Cook 116c. This series of experiments gave the highest yields of alcohol obtained heretofore on white spruce sawdust, a yield of 29.05 gallons of 190 proof or 27.6 gallons of absolute alcohol being obtained—a 29 per cent increase over the blank The results of these experiments are shown in Table V.

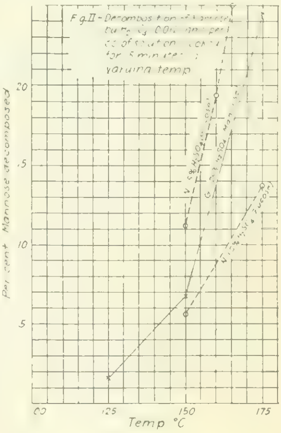
TABLE V

Cook No	Time Min.	Pressure Lbs./Sq In.	H_2SO_4 in Per cent of Dry Wood	Total Per cent Reducing Sugars	Per cent Sugars Fermentable	Alcohol Yield Per cent	Gallons Alcohol per Ton of Dry Wood
110c	15	80	7.5	21.44	13.40	6.85	20.70
111	15	100	7.5	22.51	15.12	7.72	23.40
112	15	120	7.5	23.60	17.80	9.11	27.60
116c	15	125	7.5	22.29	16.05	8.11	24.55

TABLE VI

Cook No	Time Min	Average Pressure Lbs./Sq. In	Average Temperature ° C.	H_2SO_4 Concentration G./Cc.	Per cent Mannose: Before Cook	After Cook	Decomposed	Undecomposed
1M	15	19.6	125	0.0125	3.644	3.588	1.54	98.46
2M	15	115.1	175	0.0125	3.752	3.786	-0.91	100.96
3M	15	115.1	175	0.0125	1.9152	1.156	24.55	75.45
4M	10	115.1	175	0.0125	1.9180	1.312	14.50	85.5
5M	15	54.6	150	0.0125	1.882	1.403	6.82	93.18
6M	15	19.6	125	0.0250	1.908	1.489	2.45	97.55

Since these results indicate a marked decomposition of the sugars under rather extreme conditions, the question naturally arose as to what sugars were the most susceptible to variations of conditions. Neuman[4] studied the decomposition of glucose by dilute acid at different temperatures and concluded that 175° C. marked the "critical point" beyond which it is useless to investigate the production of sugars. Since mannose constitutes a considerable proportion of the sugars that result from the hydrolysis of softwoods, it was desirable to repeat this series of experiments upon this sugar. The results obtained are given in Table VI and Fig. II. In the case of mannose 1.25 per cent sulfuric acid was used as compared with 1.0 per cent and 1.5 per cent in Neuman's work. The decomposition of mannose under similar conditions is apparently the same as that of glucose, since the curve showing the rate of decomposition parallels those of glucose.



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[8] U. S. Dept. Agr., Bull. 983.

[4] Dissertation, Dresden, 1910, p. 31.

Report of Committee on Fertilizer Legislation

A report of the Committee on Fertilizer Legislation of the Division of Fertilizer Chemistry of the AMERICAN CHEMICAL SOCIETY was presented at the Milwaukee meeting by J. E. Breckenridge. This report consisted of a review of the fertilizer legislation of importance enacted during the past year, referring particularly to the new Florida law relating to the guarantee of available and soluble nitrogen, and to the new North Carolina law pertaining to the showing of the mineral and organic nitrogen on the source tags.

Partial Hydrolysis of White Spruce Cellulose[1]

By E. C. Sherrard and G. W. Blanco

FOREST PRODUCTS LABORATORY, MADISON, WIS.

DURING the investigation of the hydrolysis of spruce cellulose, attention was directed to the presence of considerable quantities of easily hydrolyzable material contained in cellulose prepared by the Cross and Bevan method. That this material is not present as such but is produced by mild hydrolysis is indicated by the fact that, although after isolation it is extremely soluble in water, it can be removed from the cellulose only upon prolonged boiling with water. It has been obtained in the form of a white powder by concentrating the water extract to a thick sirup and precipitating with ethyl alcohol. This powder has a relatively small reducing value and gives no test for mannose. After hydrolysis with dilute acids, however, the reducing value is increased to about five times that of the original and a sharp test for mannose is obtained. Pentoses are also present in considerable quantity.

This solid material has been partially purified by dissolving in water and fractionally precipitating with alcohol. The product so obtained is so extremely soluble in water that when exposed to the air the particles or crystals coalesce and finally liquefy. Some doubt exists at this time as to the nature of the material, since on two occasions well-formed, needle-like crystals were present when examined under a low power microscope in the presence of the mother liquor. While under examination these needles would absorb water and completely dissolve. Subsequent attempts to purify further by repeated reprecipitations resulted in obtaining the material in an extremely fine powder. Upon long standing, needles again appeared but they constituted only about one-half of the total powder, the remainder consisting of the fine transparent particles noted above. The fine material showed the same tendency to dissolve when exposed to air or moisture.

The presence of this water-soluble material in the cellulose was at first ascribed to a mild hydrolysis by residual acetic acid during drying. As a consequence, a new quantity of cellulose was prepared and hydrolyzed immediately after the final chlorination both before and after drying. A second portion was treated with acetic acid in the usual way and then hydrolyzed before and after drying. A third sample had the acetic acid removed by washing with dilute ammonium hydroxide and drying. The results of these experiments are given in Table I. It will be noticed that drying has the most pronounced effect in increasing the water-soluble material as indicated by the loss in weight of the cellulose. Treatment with acetic acid without subsequent drying decreases the water-soluble, but after drying an increase is obtained. The removal of acetic acid by ammonia decreases the yield quite markedly. The reducing values given in terms of dextrose agree quite well with the quantity of cellulose lost upon hydrolysis, except that after acetic acid treatment the reducing value of the water-soluble material is increased. Successive refluxing indicated that not all the material is removed until after the third 4-hour treatment with boiling water. The ratio of reducing values of the water-soluble material before and after hydrolysis varies from 1:2 to 1:5, and indicates that partial hydrolysis occurred during extraction or that the material is not homogeneous. The ratio of mannose to total reducing material is fairly constant in Experiments 1 and 5, but Experiment 2 indicates that hydrolysis is more complete after drying, while 6B indicates additional hydrolysis by the combined action of acetic acid and heat.

Two samples of the water-soluble material were prepared in the form of a white powder and were subjected to an examination, the results of which are given in Table II. The reducing values are given in terms of dextrose. Sample 1 was prepared in the usual way, while Sample 2 was washed with about 20 liters of boiling water to make sure that no water-soluble material remained in the cellulose.

TABLE I—EXPERIMENTS ON THE REFLUXING OF WHITE SPRUCE CROSS AND BEVAN CELLULOSE WITH WATER FOR 4 HOURS

					EXAMINATION OF WATER EXTRACT							
					Before Hydrolysis with 4.5% H_2SO_4			After Hydrolysis with 4.5% H_2SO_4				
Expt.	Condition of Cellulose	TREATMENT	Cellulose Extracted Per cent of Original	Total Cellulose Extracted Per cent of Original	Per cent of Reducing Material	Reducing in Per cent of Cellulose Removed	Total Reducing Material Per cent of Total Cellulose Removed	Per cent of Reducing Material	Reducing Material in Per cent of Cellulose Removed	Reducing Material in Per cent of Total Cellulose Removed	Mannose Per cent of Original Cellulose	Mannose Per cent of Total Reducing Material
1	Wet	First refluxing with water. Before acetic acid treatment..	13.95	13.95	1.00	7.17	. .	5.00	35.84	...	1.17	23.40
3	Dry	Refluxing of residue from Expt. 1.......	7.62	21.57	0.62	8.14	7.51	3.13	41.07	37.70	...	...
4	Dry	Refluxing of residue from Expt. 3.......	1.28	22.85	...	...	...	...	...	...	...	...
2	Dry	First refluxing with water. Before acetic acid treatment......	21.80	21.80	3.01	13.80	13.80	8.21	37.64	...	3.80	46.16
5	Dry	Refluxing of residue from Expt. 2.......	5.87	27.61	1.28	21.80	15.50	4.51	77.00	46.00	1.26	28.00
6A	Wet	First refluxing after acetic acid treatment	6.80	6.80	3.15	46.32	...	6.60	97.25	...	2.13	32.30
7	Dry	Cellulose after acetic acid treatment, washed with 1 per cent NH_4OH and refluxed with water....	4.08	4.08	0.34	8.33	8.33	2.30	56.37	...	...	. .
6B	Dry	First refluxing after acetic acid treatment...... ...	16.24	16.24	3.96	24.38	...	7.49	46.12	...	4.97	66.30
9	Dry	Residue from Expt. 6B	4.72	20.96	0.93	17.58	23.40	3.25	...	...	...	...
10	Dry	Residue from Expt. 7	1.54	6.62	Trace	...	..	1.15	74.67	52.11	...	. .
11	Dry	Residue from Expt. 6A	7.15	13.95	1.00	14.00	29.03	3.28	45.87	70.83	.	...
12	Dry	Hydrolysis of cellulose residue from Expt. 9 with 5% HCl.....	21.72	42.68	...	...	...	14.88(HCl)	68.51	60.03	3.20	...

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[1] Presented before the Division of Cellulose Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

TABLE II—REFLUXING OF CROSS AND BEVAN CELLULOSE-WATER EXAMINATION OF PRECIPITATED MATERIAL

DETERMINATION	Sample 1 Per cent	Sample 2 Per cent
Cellulose removed	16.56	11.00
Precipitated material	12.57	12.03
Reducing material before hydrolysis	15.96	11.20
Reducing material after hydrolysis, 4.5% H_2SO_4	70.73	57.21
Mannose in per cent of sample	33.37	27.00
Mannose in per cent of total reducing material	47.18	47.00
Pentose in per cent of sample	19.30	21.58
Pentose in per cent of total reducing material	27.28	37.70

The yield of 12 per cent water-soluble material corresponds approximately with the loss in the preparation of α-cellulose and is a trifle less than the loss in cellulose. The material upon ignition leaves no ash, is insoluble in alcohol, chloroform, acetone, methanol, and benzene. The melting point is not definite but the material begins to darken at 220° C.; at 235° C. it turns dark and begins to decompose. It shows no reaction with phenylhydrazine. The quantity of pentose contained corresponds to 37.4 per cent of the pentose present in the original cellulose. The mannose content of the powder corresponds to 42.8 per cent of that contained in the original cellulose.

No attempt is made at this time to ascribe a definite chemical constitution to this material. Were it not for its apparently crystalline form, it might well be considered a mannan. Further investigation of this material is now under way.

The Estimation of Pentoses and Pentosans[1,2]

I—The Formation and Distillation of Furfural

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Following a review of previous work on the formation of furfural, Part I is a study of the factors influencing the production of furfural from pure arabinose, pure xylose, gum arabic, and pine sawdust. A method for distilling pentoses from acid solution by steam is described, in which theoretical yields of furfural are discussed.

Part II, which will appear in a subsequent issue, describes several new volumetric methods for the determination of furfural in aqueous solution, and includes a bibliography on pentoses and pentosans.

THAT the wide distribution of the pentosans in nature, as pointed out by Tollens in 1891, may be of considerable significance in plant economy, is indicated by the work of Spoehr, Hooker, and Rosa. These substances also constitute a large portion of the nitrogen-free extract of many animal feeds and have been the subject of numerous experiments in animal metabolism. (McCollum and Brannon, Swartz.) The pentosan determination has also been used as a basis for determining the degree of milling of flours (Gerum). It is apparent, then, that a convenient and accurate method for estimating these substances is very necessary. Because of the serious shortcomings inherent in the official method for determining pentosans, the present work was undertaken.

HISTORICAL

FORMATION OF FURFURAL—Döbereiner (1832) first obtained furfural by the distillation of sugar with pyrolusite and sulfuric acid. Stenhouse (1840) later showed the pyrolusite to be unnecessary, while Völckel (1853) found that furfural was a decomposition product of many carbohydrate materials. Stenhouse (1850) was the first to prepare furfural on any appreciable scale. He distilled wheat bran with strong sulfuric acid. The use of a strong solution of zinc chloride in the distillation procedure was proposed by Babo (1853). Stone and Tollens (1888) and Wheeler and Tollens (1889) used sulfuric acid of various concentrations. Phosphoric acid was tried by Mann, Krüger, and Tollens (1896). Glacial acetic acid was used by Testoni (1917). It was early recognized, however, that the use of 12 per cent hydrochloric acid gave better yields of furfural, in a shorter time, with more accurate duplication of results, and with less "humin" formation, than when any other acid was used [Allen and Tollens (1890), Günther and Tollens (1890), de Chalmot and Tollens (1891), Councler (1892), Stone (1897), Hauers and Tollens (1903), Jolles (1905), Ling and Nanji (1921)]. Moreover, even acid of 12 per cent concentration has an appreciable destructive effect on furfural, as shown by Fraps (1901), Jolles (1905), Mayer and Tollens (1907), and van Haarst and Olivier (1914), and also upon pentose as argued by Unger and Jäger (1903), and Fraps (1915). Also, araban and fucosan, as well as the corresponding sugars, produce furfural very slowly so that the yield from them is lower than that from others of the group due to the destructive action of the acid, as has been shown by the above-mentioned writers and by Kunz (1916). The yields of furfural usually obtained are recorded in Table I.

TABLE I—YIELDS OF FURFURAL OBTAINED FROM PENTOSE SUGARS BY DISTILLATION WITH ACIDS

Pentose Recovery Per cent	Yield of Furfural Per cent	OBSERVER
	Arabinose	
75.00	48.00	Browne (1912)
74.32	47.56	Unger and Jäger (1903)
74.54 to 82.35	47.7 to 52.7	DeChalmot and Tollens (1891)
73.44	47.00	MacKenzie (1913)
100	64.00	Ling and Nanji (1921)
98.7 to 100.8	64.00	Jolles (1905)
	Xylose	
89.85	57.50	Unger and Jäger (1903)
90.00	57.60	Browne (1912)
87.5 to 92.2	56 to 59	DeChalmot and Tollens (1891)
97.5 to 100.3	64.00	Jolles (1905)

Substances other than pentose may also yield furfural on distillation with acid. Glucuronic acid is one of these, and Tollens (1909) has determined it by a method identical with that for pentoses. However, glucuronic acid is rarely encountered. It has also been claimed that oxycellulose produces furfural. This statement appears to be based on the early work of Cross, Bevan, and Beadle (1894), Vignon (1899), and Faber and Tollens (1899), which was done before the production of hydroxymethylfurfural from hexose materials was established. Moreover, much of the furfural said to be produced from cellulose may really have its origin in true pentosans (hemi- and ortho-pentosans) contained in the cellulose. [König and Rump (1914), Schwalbe (1918), Heuser and Haug (1918), Schwalbe and Becker (1920).] Other interfering substances have been mentioned, but little is known concerning their composition and distribution. Bray and Staidl (1922) claim to have worked out a correction to lessen the error due to these substances, but have not published it.

TESTS FOR FURFURAL—For determining when distillation is complete, aniline acetate has usually been used. This is prepared by adding glacial acetic acid to a mixture of equal parts of colorless aniline and water until the mixture suddenly clears. It has been frequently observed, however, that acetic acid often gives a positive test, due to the presence in it of furfural, as was shown by V. Meyer (1878). To avoid the difficulty, the use of

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concentrated hydrochloric acid has been recommended by Tolman and Trescott (1906), Cunningham and Doree (1914), and Schorger (1917); but strong mineral acids may destroy the color, as has been argued by de Chalmot (1893) and by Baker and Hulton (1916). Hydroxymethylfurfural, arising from hexoses during acid distillation, does not interfere, since it is formed so slowly and in such small quantities [van Ekenstein and Blanksma (1910), Cunningham and Doree (1914)]. Jolles (1905) believed the aniline test was not sufficiently sensitive, and used Bial's orcinol-ferric chloride test solution. Van Haarst and Olivier (1914) preferred phloroglucinol. The present official method for the determination of pentoses makes no mention of the use of an indicator. Distillation is simply carried out at a definite rate until a definite volume of distillate has been received.

Official Method and Suggested Modifications

The official method of distillation is to heat the sample with 12 per cent hydrochloric acid at such a rate that 30 cc. pass over in 10 minutes. Thirty cubic centimeters more of 12 per cent acid are then added and the process is repeated until 360 cc. of distillate have been collected.

The following modifications have been proposed:

Cross, Bevan, and Smith (1895) suggested the use of the constant level apparatus of Chorley (1895), and Stanek (1900) devised an automatic apparatus to facilitate the procedure, but these have not come into use. Heuser (1921) found that higher and more accurate yields of furfural were obtained if the weighed sample of pentosan was dissolved in normal sodium hydroxide solution before distilling with acid. Dekker (1914) added 500 cc. of 12 per cent hydrochloric acid and distilled directly. His results were low. Grund (1902) added and distilled in 50-cc. fractions and recorded a more intensive action by the change. Jolles (1905) added the acid, and steam-distilled the hydrolysate, heating the latter so that its volume decreased to about half while 800 cc. of water were distilled through it. More acid was then added and the process repeated until no more furfural was produced. Jolles claimed to get theoretical conversions of pentoses (arabinose and xylose) to furfural, the only such claim made in the literature.

Experimental

Materials—The following pentose materials were used:

l-Arabinose, $[\alpha]^{20}_{D} = 103.77°$
d-Xylose, $[\alpha]^{20}_{D} = 18.81°$

As pentosan-containing materials, pine sawdust and gum arabic were used, each being ground to 50 mesh. These materials were distilled with acid according to the procedures outlined below and the furfural-containing distillate was titrated by the method proposed in Part II, which is briefly as follows:

Method of Determining Furfural—A small aliquot of the distillate was titrated with standard alkali to determine its acidity. This aliquot was then re-added to the distillate and sufficient hydrochloric acid or strong sodium hydroxide solution also added to give a final acidity of about 4 per cent. Ten cubic centimeters of 20 per cent potassium bromide were then added and the resulting solution was titrated with standard potassium bromate solution in the manner described in Part II.

Indicator—For deciding when distillation was complete, strips of filter paper were used which had been dipped in aniline hydrochloride solution and dried. The aniline hydrochloride solution was freshly prepared from colorless aniline and C. P. hydrochloric acid.

Effect of Acidity during Distillation—Owing to the ease with which furfural is destroyed by strong acid, a study of the acidities obtained during distillation was regarded essential. Two 12 per cent hydrochloric acid distillation procedures were studied—(1) the method of the Association of Official Agricultural Chemists (1920), which has been said to yield low furfural figures; and (2) the method of Jolles, in which theoretical yields were claimed. In both studies the boiling point temperatures were taken as an index to the concentration of acid present in the distillation flasks.

Official Distillation Procedure—The samples were distilled as directed in the official method until 360 cc. had distilled over. In each instance the distillation began at 103° to 104° C., but had reached 108.55° C. (corrected) by the time 60 cc. had been distilled out. Subsequent additions of 12 per cent hydrochloric acid caused a temporary drop of 0.6° C., but the constant boiling temperature was very soon again reached. The greater part of the distillation took place, therefore, from acid of 18 to 20 per cent concentration. The data are recorded in Table II. The furfural in the distillate was determined by the titrimetric method described in Part II of this paper.

Table II—Pentose Determinations Distillations by the Official Method
(Volume of distillate, 360 cc.)

Weight of Sample Gram	0.1 *N* $KBrO_3$ Cc.	Pentose Found (Factor = 0.007505) Gram	Recovery Per cent
		Arabinose	
0.2016	25.50	0.1914	94.9
0.2005	25.75	0.1943	96.8
0.2020	25.35	0.1903	94.2
0.2045	26.00	0.1951	95.4
		Average	95.3
		Xylose	
0.2038	26.00	0.1951	95.7
0.2022	25.75	0.1943	96.1
0.2016	25.80	0.1936	96.0
0.2009	25.75	0.1943	96.7
		Average	96.1

It will be noted that a recovery of 95.3 per cent from arabinose and 96.1 per cent from xylose was secured. These values are higher than have been found by most workers with the exception of Jolles (1905), and (possibly) Ling and Nanji (1921). Both Jolles and Ling and Naji, as well as the writers, used titrimetric methods for determining the furfural. If the higher results which the writers obtained are not due to a more accurate method of determining the furfural in the distillate, they are at a loss to explain their high values, especially those of arabinose.

Table III—Pentose Determinations. Distillations by Steam from 12 and 20 Per cent Hydrochloric Acid Solutions

Per cent Acid	Weight of Sample Gram	Volume of Distillate Cc.	0.1 *N* $KBrO_3$ Cc.	Pentose Found (Factor = 0.007505) Gram	Recovery Per cent
		Arabinose			
12	0.2030	715	27.00	0.2026	99.8
	0.2020	650	27.00	0.2026	100.3
	0.2014	900	26.80	0.2011	99.9
	0.2005	1200	26.70	0.2004	99.9
20	0.2030	1250	26.75	0.2008	100.2
	0.2040	755	26.75	0.2008	100.2
	0.2000	900	26.75	0.2008	100.3
	0.2010	1050	26.75	0.2008	99.9
				Average	100.1
		Xylose			
12	0.2003	400	26.65	0.2000	99.8
	0.2010	620	26.75	0.2008	99.9
	0.2040	1000	27.00	0.2026	99.3
	0.2020	425	26.85	0.2015	99.7
20	0.2035	300	27.25	0.2045	100.4
	0.2045	375	27.25	0.2045	100.0
	0.2033	500	27.15	0.2038	100.2
	0.2016	825	26.80	0.2011	99.8
				Average	99.9

Distillation Method of Jolles—Jolles advised that the pentose sample be placed in a distilling flask with 200 cc. of 12 per cent hydrochloric acid and steam-distilled, boosting at such a rate that the volume decreased to about 100 cc. while the steam from 800 cc. of water was led through it. More 12 per cent hydrochloric acid was then added, and the process repeated as long as furfural was produced. The temperatures obtained during this type of distillation were always from 103° to 104° C., which indicated that the acidity of the hydrolysate remained in the neighborhood of 12 per cent throughout the distillation. The lack of destruction of furfural observed by Jolles must then be due either to the low acidity during distillation, or to the prompt removal of the furfural by the current of steam passing through, or both.

To determine which of these factors was the more important, samples of pure pentoses and of the pentosan materials mentioned above were distilled with steam from both 12 and 20 per cent hydrochloric acid. The heat was adjusted so that temperatures of 103° to 104° C. were maintained in the 12 per cent distillation, while temperatures of 107° to 108° C. were held in the 20 per cent distillations. Within the limits of experimental error, theoretical results were in all cases obtained from the pentoses used, regardless of the concentration of acid. This is shown in Table III. The pentosan materials gave constant yields, indicating that no loss of furfural had occurred. (Table IV) Furthermore, the rate of distillation did not affect the yield, as shown by the marked differences in volumes of distillates obtained. Evidently, even a slow current of steam is sufficient to sweep out the furfural as fast as it is formed from the pentoses.

TABLE IV—PENTOSAN DETERMINATIONS DISTILLATIONS BY STEAM FROM 12 AND 20 PER CENT HCl SOLUTIONS

Per cent Acid	Weight of Sample Grams	Volume of Distillate Cc.	0.1 *N* $KBrO_3$ Cc.	Pentosan Found (Factor = 0.006605) Gram	Pentosan Per cent
		Gum Arabic			
12	0.5018	820	24.50	0.1618	32.2
	0.5033	1160	24.25	0.1602	31.8
	0.5053	725	24.65	0.1628	32.2
	0.5016	925	24.40	0.1611	32.1
20	0.5004	640	24.25	0.1602	32.0
	0.5053	685	24.50	0.1618	32.0
	0.5047	940	24.50	0.1618	32.1
	0.5036	900	24.50	0.1618	32.1
				AVERAGE	32.1
		Sawdust			
12	1.0020	935	23.25	0.1535	15.3
	1.0017	875	23.25	0.1535	15.3
	1.0056	1000	23.35	0.1542	15.3
	1.0064	900	23.50	0.1552	15.4
20	2.0020	615	46.40	0.3064	15.3
	2.0014	710	46.25	0.3054	15.3
	2.0049	625	46.50	0.3071	15.3
	2.0032	600	46.50	0.3071	15.3[a]
12	1.0026	575	23.00	0.1519	15.1[a]
	1.0077	870	23.25	0.1535	15.2[a]
	1.0018	530	23.25	0.1535	15.3[a]
				AVERAGE	15.3

[a] These distillations were carried out according to Heuser's method (1921), the samples being macerated with 4 per cent sodium hydroxide before distilled with acid. No increased yield of pentosan was obtained. Heuser's determinations always ran 4 per cent higher by this treatment. Hence the foregoing data further substantiate the claim that theoretical yields of furfural are obtained from pentosans by the proposed distillation procedure.

A comparison of the pentose results in Tables II and III indicates that the reason low results are obtained by the official method is that some of the furfural is destroyed by long contact with strong acid. Moreover, this destructive effect can be entirely eliminated by carrying a slow current of steam through the hydrolysate, thereby removing the furfural as fast as it is produced. Hence the following method for the quantitative production of furfural from pentose materials is proposed.

PROPOSED METHOD FOR DISTILLATION OF PENTOSES—Place a weighed (0.20 to 5.0 grams depending upon the pentose or pentosan content) sample of the material, and 200 cc. of 12 per cent hydrochloric acid (specific gravity, 1.06) in a 750-cc. distilling flask fitted up for steam distillation. Conduct a slow current of steam into the mixture and as soon as the mixture reaches the boiling temperature heat the distilling flask with a low flame so that the boiling temperature remains between 103° to 105° C. as measured by a thermometer inserted in the vapor in the neck of the distilling flask. By observing this precaution the addition of fresh acid will rarely be required. About one-half of the original volume of liquid should remain in the flask at the end of the distillation. Continue distillation until a drop of the distillate no longer gives a red coloration with aniline test paper on being allowed to stand 3 to 5 minutes.

By following this procedure theoretical yields of furfural have been obtained from all the pure pentose materials which have been tested. Representative data are found in Table V.

TABLE V—PENTOSE DISTILLATIONS BY THE PROPOSED METHOD

Weight of Sample Gram	0.1 *N* $KBrO_3$ Cc.	Factor = $\frac{\text{Grams Pentose}}{\text{Cc. } 0.1\ N\ KBrO_3}$
	Arabinose	
0.2000	26.50	0.00755
0.2005	26.50	0.00755
0.2015	26.75	0.00753
0.2021	26.85	0.00752
0.2030	27.00	0.00752
0.2025	27.00	0.00750
0.2037	27.25	0.00747
0.2040	27.25	0.00748
	AVERAGE	0.007515
	Xylose	
0.3020	40.00	0.00755
0.3035	40.30	0.00753
0.3010	40.00	0.00752
0.3027	40.30	0.00751
0.3040	40.45	0.00754
0.3070	41.00	0.00749
0.3082	41.20	0.00749
0.3044	40.50	0.00752
	AVERAGE	0.007519
	TOTAL AVERAGE	0.007517
	THEORETICAL	0.007505

CONCLUSIONS

The data presented seem to warrant the following conclusions:

1—Distillations of pentose materials, carried out according to the method of the Association of Official Agricultural Chemists, take place from hydrochloric acid of 18 to 20 per cent concentration, instead of from 12 per cent acid as usually stated.

2—Hydrochloric acid of this concentration has a considerable destructive effect on furfural, and is no doubt partly responsible for the low yields of furfural that are obtained from all pentoses when the official method is used.

3—The passage of a slow current of steam through the distillation mixture is sufficient to carry the furfural off as rapidly as it is formed, thereby avoiding the destruction of furfural by long contact with strong acid.

Motion Pictures to Show Cotton Dusting Method

Two thousand feet of "movie film" were recently made by the motion picture office of the Department of Agriculture, showing the method of spreading calcium arsenate dust over fields of cotton by airplane for control of the boll weevil. The pictures were taken at Tallulah, La., where the experiments in cotton dusting by airplane are being conducted under the direction of B. R. Coad, in charge of the Delta Laboratory there.

Results obtained by this method of spreading the poison have been sufficiently satisfactory to give promise of the use of airplanes on a commercial scale in fighting the boll weevil, and the film was made largely for the purpose of creating an interest in further development of detail and to show the progress already made. It will be shown first before officials of the Department of Agriculture and of the War Department, which is coöperating in the tests by supplying the air machinery and personnel.

The best results to be obtained in spreading the poison in this manner are to be had by early morning flights when the air is still and there are no air pockets to make flying more dangerous. Three days were taken to complete the making of this negative and ten flights of from 10 to 30 minutes each were made. The planes used were two De Haviland bombers which have a speed of from 90 to 100 miles an hour.

McBain Tells Boston Chemists about Soap

A number of chemists of the Northeastern Section met James W. McBain of the University of Bristol, England, at luncheon on Monday, October 15. With J. F. Norris of the Massachusetts Institute of Technology as toastmaster, greetings were tendered the guests by A. B. Lamb of Harvard, H. P. Talbot of the Massachusetts Institute of Technology, L. C. Newell of Boston University, and L. C. Pratt of the Merrimac Chemical Company. In the evening Professor McBain addressed the regular monthly meeting of the Northeastern Section on "A Study of Soap Solutions and Its Bearing on Colloid Chemistry." Supported by many fine microphotographs, the speaker argued convincingly that a soap gel has a filamentary or "brush-heap" structure.

Charts for Estimating Temperature Distributions in Heating or Cooling Solid Shapes[1]

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This paper is abstracted from a more complete exposition entitled "On the Heating and Cooling of Certain Solid Shapes," a special paper by one of the writers deposited in the library of the Massachusetts Institute of Technology through the courtesy of the Chemical Engineering Department. In the original it has not been possible to go exhaustively into the effect of time-temperature relations upon the physical properties of the materials mentioned. Some of these relations are fairly well understood. A better knowledge of time-temperature relations in such processes as the vulcanizing of rubber, the hardening of steel, or the annealing of glass in conjunction with graphical application of the formulas of heat diffusion may help to realize Fourier's wish expressed in the introduction of the memoir, "Theorie du mouvement de la chaleur dans les corps solides (1812)," that his mathematics be applied to industry.

In many technical processes large solid shapes are subjected to temperature changes in order to attain certain physical or chemical results. In so doing the temperature-time relations, irrespective of what point may be taken as the time origin, may differ considerably and in consequence cause to exist different degrees of physical inhomogeneity. Technical examples that may be cited are found to abound in rubber, steel, glass, and other industries.

The temperature-time relations in the interior of solid bodies which are either being heated or cooled may be empirically determined by inserted thermometers, thermocouples, or other temperature-measuring apparatus, or may be calculated from the assumed conditions, in conjunction with the physical constants of the materials, the surrounding contours, shapes, and media. The fact that thermal physical data are not so complete as they might be, or that technical conditions can rarely be made to coincide with the theoretical prototypes, does not negative the value of such estimations, but does require that the precision of the computed results should not be overestimated. Where empirical observations and theoretical calculations may be made concurrently, new physical constants may be determined which will be found to be more reliable in predicting other time-temperature relations under different, though similar conditions.

The curves in Figs. 1, 2, 3, 4, and 5 were obtained by converting some of the more common formulas for heat diffusion into expressions containing pure ratios or nondimensional variables only, thereby enormously reducing the necessary basic calculations as well as extending the field of applicability.

In Figs. 1 to 5, the abscissas 0 to 5.5 are in units obtained by multiplying time, t, into the thermal diffusivity, h^2, of the material, and then dividing this product by the square of some linear dimension of the shape in question, such as the radius of the sphere or cylinder, or by one-half the thickness of the slab, R^2. The expression generally employed in denoting this relation is $\tau = th^2/R^2$, where the symbols employed are in the order mentioned.

The ordinates 1 to 0.002 refer to the ratios of unaccomplished temperature change to the total, limiting, or maximum possible temperature change that the thermal environment can impress upon any part of the body—that is, the temperature at the start is conceived to be unit and to approach or eventually become zero. At any time, t, in question the temperature is conceived to differ from the final temperature by a temperature ratio, Δ, which approaches zero as a limit. The ordinates are functions of two other variables besides time. The first variable, ρ, is the ratio of the distance from the center, axis, or midplane to the point in question to the distance from the surface to the axis, center, or midplane. This ratio, ρ, is therefore zero at the center, axis, or midplane, and unit at the surface, with intermediate values at points between. In Fig. 5, dealing with the semi-infinite solid, only the point in question is considered; hence, ρ is not involved.

The other function, m, is the ratio of the thermal conductivity, k, of the material to the product of the thermal surface conductivity, E, into the radius, R, or semithickness of the shape. This is expressed symbolically by $m = k/ER$. If the surface emissivity is infinity, $E = \infty$. That is, if the surface of the body instantly assumes the temperature of

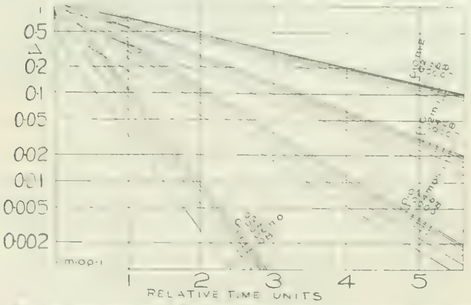

Fig. 1—Unaccomplished Temperature-Change Ratios of a Slab Initially at Uniform Temperature and Approaching Another Uniform Temperature. ρ Defines Relative Distance from Midplane; m Defines Relative Surface Resistivity

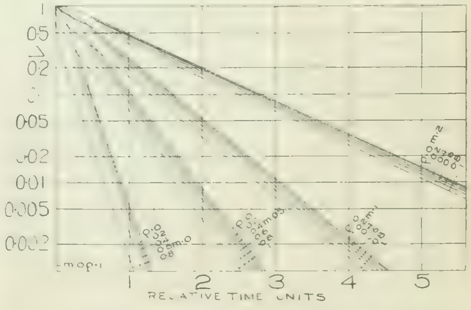

Fig. 2—Unaccomplished Temperature-Change Ratios of a Cylinder Initially at Uniform Temperature and Approaching Another Uniform Temperature. ρ Defines Relative Distance from Axis; m Defines Relative Surface Resistivity

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[1] Received May 25, 1923.

the surrounding media, then m = zero. If the surface is perfectly insulated ($E = 0$), then $m = \infty$. m may also be expressed as the ratio of surface thermal resistivity to the radius multiplied into the resistivity of the solid material. This follows because of the fact that these are reciprocals, respectively, of E and k.

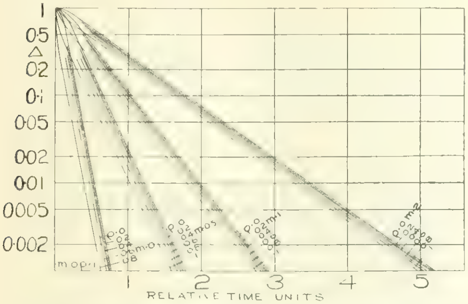

Fig. 3—Unaccomplished Temperature Change Ratios of a Sphere Initially at Uniform Temperature and Approaching Another Uniform Temperature. ρ Defines Relative Distance from Center; m Defines Relative Surface Resistivity

Figs. 1, 2, and 3 exhibit values of Δ (between 1 and 0.001) from $\tau = 0$ to $\tau = 5.5$, for $\rho = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0, and $m = 0$, 0.5, 1, and 2. For constant values of Δ, τ is nearly linearly proportional to m; hence, interpolations up to 2 are quite safe, and since the proportionality is even closer the greater m is, extrapolation may be carried up to $m = 10$ without a greater error than usually resides in the assumed physical constants.

Fig. 4 exhibits the values of Δ for $\rho = 0$, 0.2, 0.4, 0.6, 0.8, in a slab, cylinder, or sphere, where the surface is subjected to uniform change in temperature, the total temperature change at any time, t, being considered unity.

Fig. 5 was prepared to take care of a special case of either Figs. 1, 2, or 3. This figure shows not only the relative temperatures Δ for $m = 0$, 0.5, 1, and 2, but its differential, $d\Delta/d\tau$, with respect to τ for points relatively near the surface of any type of solid body—that is, where ρ lies between 0.9 and 1.0. For lower values of ρ there would be an increasing error. In this figure $\tau = th^2/R^2$ is replaced by $\tau = th^2/X^2$, where X is the linear distance from the point in question to the surface.

To illustrate and apply these figures more definitely, three examples will be adduced, and the transformation from arithlog to arithmetic ordinates will be made.

A slab of rubber 2.5 inches in thickness (hence 3.17 centimeters from surface to midplane) is at a temperature of 80° F. uniformly distributed, and is placed suddenly in surroundings (such as a heated press) maintained at a constant temperature of 280° F., and the body is allowed to heat up. It is desired to ascertain the temperature-time relations at the midplane (where $\rho = 0$) and at a point 0.25 inch from the surface (where $\rho = 0.8$). The thermal conductivity, K, of the rubber is 0.0004 calorie per centimeter cube per second, while the surface emissivity, E, is 0.0005, and the thermal diffusivity, h^2, is 0.00087 sq. cm. per second. Under these conditions

$$m = \frac{k}{ER} = \frac{0.0004}{0.0005 \times 3.17} = 0.25$$

and at $\tau = 1$, t must equal 11,600 seconds, or 3.22 hours, in order that the following condition be satisfied:

$$1 = \frac{th^2}{R^2} = \frac{t \times 0.00087}{3.17 \times 3.17}$$

The relation between temperature Fahrenheit, Θ, and Δ may be graphically determined by connecting points $\Delta = 1$, $\Theta = 80°$ F., and $\Delta = 0$, $\Theta = 280°$ F., by a straight line or by relation

$$\Theta = 280 - \Delta(280 - 80)$$

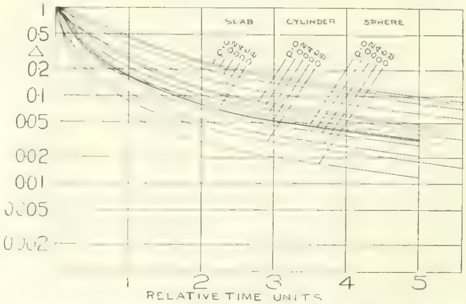

Fig 4—Unaccomplished Temperature Change Ratios at Points in a Slab Cylinder or Sphere Initially at Uniform Temperature but with Surface Temperature Uniformly Varying from Initial Value

In Fig. 6, upper part, Fig. 1 is duplicated for $\rho = 0$ and $\rho = 0.8$, and $m = 0$ and 0.5. New dotted lines for $m = 0.25$ are drawn between $m = 0$ and $m = 0.5$, interpolating proportionally between intersections of these lines and lines of constant Δ. At the right the ordinates are renumbered in terms of temperature Fahrenheit. In Fig. 6, lower part, these dotted lines are converted into solid lines on arithmetic ordinates.

A large ingot of steel is suddenly cooled at its surface from 1100° to 100° F., hence undergoing a drop in temperature of 1000° F. It is desired to ascertain the time-temperature rate of change relations at a distance of 1 cm. from the surface, assuming the thermal diffusivity of steel to be 0.15 sq. cm. per second.

At $\tau = 1$, expression $\tau = th^2/X^2$ is satisfied if $t = 6.35$ seconds, and in place of $d\Delta/d\tau$, $d\Theta/dt$, 1000° F. per 6.35 seconds or 157.5° F. per second. In Fig. 7, upper part, the ordinates are correspondingly renumbered, while in Fig. 7, lower part, the relations are converted over and expressed on arithmetic ordinates. .

A slab of glass 1.5 inches thick (hence 1.9 centimeters from surface to midplane) is subjected to a uniform temperature rate of increase of 1° C. per minute starting at 20° C. and proceeding uniformly for 30 minutes so that the surface

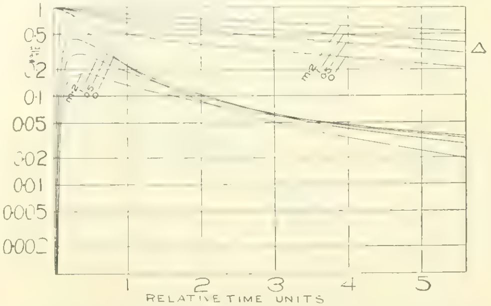

Fig. 5—Unaccomplished Temperature-Change Ratios (4 Upper Curves) with Rates of (Lower Curves) Variation per Unit of Time for a Point in a Semi-Infinite Solid Initially at Uniform Temperature. m Defines Relative Surface Resistivity

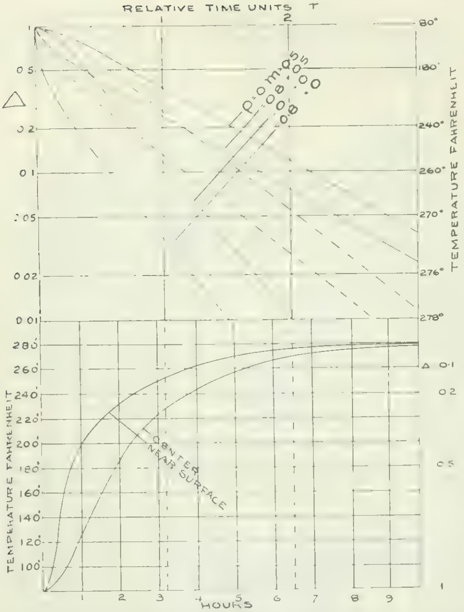

Fig. 6—Estimated Temperature Curves at the Center and 1/4 Inch from Surface of a Slab of Rubber Being Heated from 80° to 280° F.

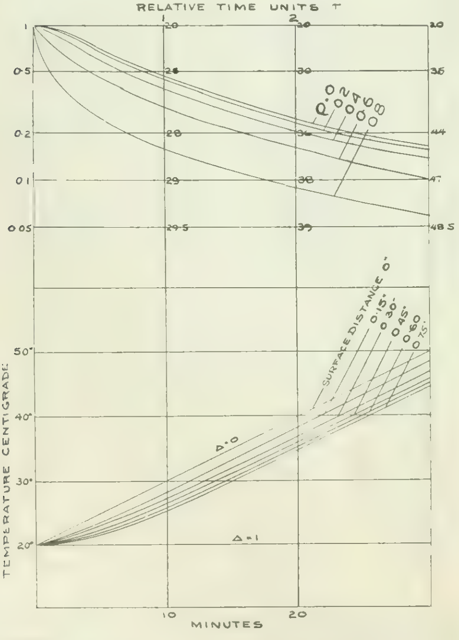

Fig. 8—Temperatures in a Glass Slab the Surface Temperature Being Raised 1° C. per Minute Starting at 20° C.

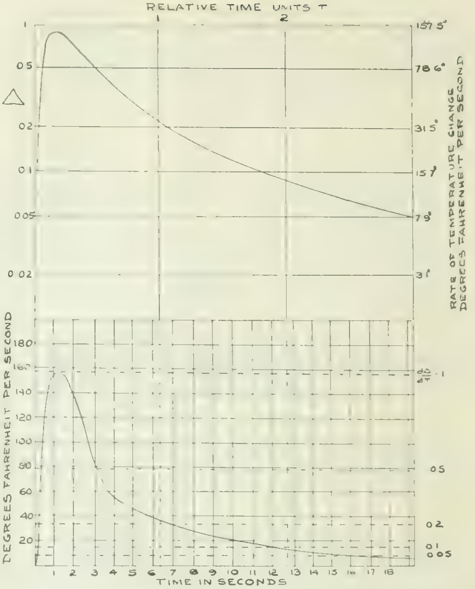

Fig. 7—Rate of Cooling in a Steel Ingot 1 Cm. from the Surface—Cooling from 1100° to 100° F.

then arrives at a temperature of 50° C. It is desired to ascertain the temperature-time relations at 0, 0.15, 0.30, 0.45, 0.60, and 0.75 inch from the surface—that is, at $\rho = 1$, 0.8, 0.6, 0.4, 0.2, and 0 from 0 to 30 minutes.

To satisfy equation $\tau = th^2/R^2$ when $\tau = 1$, t must equal 600 seconds, or 10 minutes.

Fig. 8, upper part, presents Fig. 4 renumbered at $\tau = 1$, 2, and 3 to $t = 10$, 20, and 30, at which times the surface temperatures are by definition 30°, 40°, and 50° C., where $\Delta = 1$ successively stands for 10°, 20°, and 30° C.

Fig. 8, lower part, presents the same relations on arithmetic ordinates. It will be noted here that after a short time the actual temperature differences between different layers equidistant from the midplane become uniform and the conditions approach a state of uniform flow.

It must be perfectly apparent from these examples that where temperature ratios are employed it is immaterial what temperature scale is used. In evaluation of τ in the equation $\tau = th^2/R^2$, care must be taken that h^2 is expressed in the same units as t and R^2. It should also be noted that Figs. 1 to 5, and upper parts of 6, 7, and 8 are expressed in arithlog ordinates—that is, the abscissas progress according to equal arithmetic increments, while the ordinates progress in a logarithmic order, equal increments represent equal ratio or percentage increases (or decreases). Because of the fact that many of the curves are nearly straight lines when plotted on arithlog paper, its use is particularly recommendable, especially if extrapolation is to be done. Figs. 6, 7, and 8, lower parts, are plotted on arithmetic ordinates. Both abscissas and ordinates progress by equal arithmetic increments.

On the occasion of the dedication of the Jesse Laboratory of Chemistry at Brown University on October 10, the degree of doctor of science was conferred on **James W. McBain** of the University of Bristol, who made the principal address. The degree of doctor of laws was conferred upon **James R. Angell**, president of Yale University.

Experiments on the Arc Process for Nitrogen Fixation[1]

By Edgar D. McCollum and Farrington Daniels

UNIVERSITY OF WISCONSIN, MADISON, WIS.

Liquid nitrogen peroxide may be made on a laboratory scale from air in an electric arc with the help of silica gel. No improvement in the chemical efficiency of the arc was obtained by using rapid air currents, by interrupting the arc, or by changing the character of the arc with condensers. Better yields were obtained at high voltages.

THE fixation of nitrogen by the arc process is a most alluring problem. It appeals to the research chemist because the present limits of efficiency (approximately 1 gram atom of fixed nitrogen per kilowatt-hour) are not established by theoretical deductions,[2] and because the electrochemistry of gases has received a new impetus in the recent development of the field of atomic structure. It appeals also to the industrial chemist because the raw materials—air, water, and gravity—are cheap and because the labor costs are remarkably low.

The problem can be solved and the limits of efficiency can be established only after years of fundamental research in the fields of electricity, photochemistry, and atomic structure. It seemed worth while, however, to perform a few experiments in which the variables were carefully limited in order to test out certain procedures which it was thought might increase the efficiency.

It is important to point out that in the case of stable, efficient arcs the practical problem lies in the quick removal of the nitric oxide before decomposition can set in, and it is immaterial whether the nitric oxide is formed in a purely thermal equilibrium, by electronic or ionic impact, or by photosynthesis. One of the simplest ways of quickly removing the products consists in blowing the air through the arc very rapidly. There are two limits to this procedure—first, the extinguishing of the arc, and, second, the difficulty of recovering the oxidized nitrogen when its concentration is low.

The second objection may be overcome by dispensing with the ordinary absorption towers filled with liquids and adsorbing the nitrogen peroxide with silica gel.[3] Since the cost of absorption in present practice constitutes about one-quarter of the total cost of fixing nitrogen by the arc process, the experiments seemed particularly worth while.

APPARATUS AND PROCEDURE

The apparatus is shown in Fig. 1. The chamber, *A*, was made of Pyrex glass 5 cm. in diameter and 100 cm. long. The electrodes, *E*, were placed in side tubes, fused to the main tubes. The side tubes were long enough so that an airtight joint could be made with rubber tubing without danger of heating the rubber. The air was previously dried through two washing bottles of sulfuric acid and two towers of sodium hydroxide sticks. It was introduced into the arc from below by means of a 5-mm. glass tube at right angles to the electrodes. The end of the glass tube was placed 3 mm. from the electrodes and remained in the same position throughout all the experiments. The electrodes, of 3-mm. steel rods, were touched together to start the arc and then drawn apart to a distance of 5 mm. in all the experiments. The flowmeter, *F*, was calibrated in liters of air per minute, passing into the arc.

The nitrogen peroxide was collected in a weighed tube of silica gel, *S*, 2 cm. in diameter, a tube of glass wool, *G*, serving to trap particles coming from the disintegration of the electrodes. A second tube of silica gel and a wash bottle were placed after tube *S*, but they showed at all times that the absorption in the first tube was complete. Most of the nitrogen peroxide was absorbed in the first 10 cm. of the tube, as shown by the brown color. Connections were made with overlapping glass joints and de Khotinsky cement. The increase in weight of the silica gel tube gave directly the number of grams of nitrogen peroxide. This weight was checked occasionally by heating the silica gel in a current of air. The loss in weight was always equal to the gain in weight previously observed.

The wattage throughout all the experiments was kept constant by adjusting the core of a choke coil, *C*, until the wheel of the watt-hour meter, *M*, made 6 revolutions per minute. This operation required close attention. Since each revolution of the wheel corresponded to 5/24 watt-hour, the energy input was 75 watts per hour. Most of the experiments were continued for an hour, giving usually about 1 gram of nitrogen peroxide, and the total energy consumed was read directly on the watt-hour meter. The current was measured with a hot wire ammeter in series with the arc.

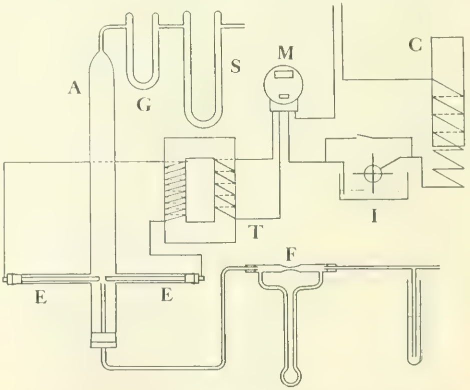

FIG. 1—APPARATUS FOR FIXATION OF NITROGEN BY ARC PROCESS

In some of the experiments an interrupter, *I*, was used. It was constructed of four stout wires arranged at right angles on a wooden hub. The wires dipped into a trough of mercury and were so arranged that the circuit was open half the time and closed half the time. The hub made 125 revolutions per minute, interrupting the arc 500 times per minute. The choke coil was set to allow the consumption of 75 watts per hour on continuous current and inasmuch as the current was flowing during only one-half of the time the experiment was allowed to run for a longer time. The actual energy consumption was read directly on the meter. In using

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[1] Received April 16, 1923.

[2] Thermodynamical calculations such as given in Haber's "Thermodynamics of Technical Gas Reactions," p. 267, are open to considerable suspicion as regards the temperature. In fact, one cannot speak properly of the temperature of an arc in a quantitative sense.

[3] McGavack and Patrick, *J. Am. Chem. Soc.*, **42**, 946 (1920)

the interrupter the air flow was such as to sweep the products of the arc away from the electrodes while the arc was extinguished. One liter of air was passed through the 5-mm. tube in 1 minute. The cross section of the tube was 0.1963 sq. cm., giving a linear velocity to the gas of 1000/0.1963, or 5102 cm. per minute. The arc was out for 0.002 minute. The gas moved 10 cm. during this time. Since the height of the arc was between 2 and 3 cm. all the gas must have been removed from the region of the arc while the current was off, even allowing for spreading out of the air after leaving the nozzle.

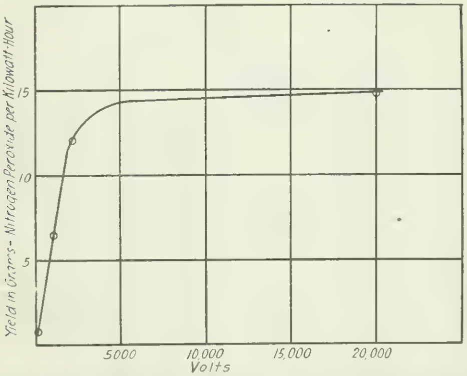

Fig. 2—Relation between Voltage and Yield of Nitrogen Peroxide

This apparatus made it possible to keep constant the energy input (75 watts per hour), the electrode material, the electrode distance, the air pressure, and the stream lines. With these variables eliminated the effect of the other factors was studied. For 110 volts the ordinary alternating current lighting circuit was connected; for 1100 and 2200 volts a 2-kilowatt, oil-immersed transformer, *T*, was used, and for 20,000 volts a Thordarson 1-kilowatt transformer served. Corrections were not made for the transformer losses, the energy input being measured on the primary side. This loss probably did not amount to more than 10 per cent. The interrupter was placed ahead of the transformer so that its losses were not included.

RESULTS

The experiments of Table I show the influence of voltage and air velocity, with an energy consumption of 75 watts per hour.

Table I—Effect of Voltage and Air Velocity on Yield

Volts	Air Flow Liters/Minute	Yield N_2O_4 Grams/Kilowatt-Hour
110	1.00	1.5
110	1.00	0.3
1100	0.48	7.5
1100	0.90	7.9
1100	0.91	7.6
1100	0.94	4.9
1100	1.00	4.8
1100	1.00	7.5
1100	Fast	5.0
1100	Fast	8.2
1100	Fast	5.0
2200	1.00	12.3
2200	1.00	12.8
2200	1.00	10.2
2200	1.00	13.3
20,000	0.95	9.0
20,000	1.00	12.8
20,000	1.00	15.8
20,000	1.10	14.4
20,000	1.30	16.1

The agreement between experiments performed under supposedly constant conditions is not entirely satisfactory, but these variations seem to be a failing common to all similar investigations, due possibly to slight fluctuations in the arc. Average values are, however, significant.

The 110-volt, 1100-volt, and 2200-volt arcs were yellow in color, but the 20,000 volt arc was whitish. The current with the 1100-volt arc was 0.7 ampere and with the 20,000 volt arc, 0.2 ampere. It is obvious that the power factor was low on account of the large amount of inductance in the circuit.

In Table II are shown the influence of various changes in the arc. In all these experiments the energy input was 75 watts per hour and the voltage 20,000.

Table II—Effect of Changes in Arc

Description of Arc	Flow Liters/Minute	Yield N_2O_4 Grams/ Kilowatt-Hour
Spark discharge	0.95	2.0
	0.97	4.8
	1.00	4.9
Small condenser, blue spark	0.95	12.8
	1.00	8.9
	Fast	8.1
Large condenser, fat blue spark	Very slow	Low
	1.00	Low
Large condenser, 115 watts, yellow	1.00	4.2
Ozonized air used, white arc	1.00	11.4
	1.00	14.7
Interrupted arc, white	0.95	17.4
	1.00	15.9
	1.00	14.0
	1.00	13.5
	1.00	13.4

With large electrodes the yields decreased, and in fact with electrodes of too large cross section the thermal conduction was so great as completely to prevent the maintenance of an arc at the low wattages. If the electrodes were too small, on the other hand, they were melted by the arc. Terminals of stout platinum wire were fused at once.

Several experiments with direct current at 110 volts gave low yields which were about the same as those with the alternating current at 110 volts.

Since the second silica gel tube showed no increase in weight, it was assumed that the recovery of the fixed nitrogen was complete. The first silica gel tube returned to its original weight after heating to 350° C., in a slow stream of air (1 or 2 cc. per minute), and no nitric acid was observed either in the connecting tubes or in the tube surrounded by ice and salt in which the nitrogen peroxide was liquefied. These facts showed that all the fixed nitrogen was removed as nitrogen peroxide, even though some nitric acid may have been formed from the water on the silica gel.

The most important feature of the investigation consisted in keeping the energy input constant throughout the experiments. The maximum yield of 16 grams of nitrogen peroxide, or 22 grams of nitric acid per kilowatt-hour, is only about a third of the yield frequently obtained with large arcs in industrial practice.

CONCLUSIONS

Adsorption with silica gel offers an excellent method for the recovery of oxides of nitrogen from the arc, since in this way nitrogen peroxide may be removed from rapid air currents at low concentrations. By heating the silica gel the concentrated nitrogen peroxide may be recovered ready for liquefaction, or for absorption in water to give concentrated nitric acid. The silica gel is then ready for further adsorption.

The yield of nitrogen peroxide per kilowatt-hour increases rapidly with the voltage up to a few thousand volts, after which further increase in voltage does not greatly affect it. The relation between voltage and yield per kilowatt-hour, for an energy input of 75 watts per hour in the apparatus described, is shown in Fig. 2. The curve is roughly of the exponential type and is similar to saturation curves obtained in certain ionization experiments. It suggests that possibly an increase in voltage increases the fraction of energy which can be made to do chemical work, but that some other influence, such as concentration, or possibly an intermediate step of slow velocity, limits the production for the larger yields.

Small variations in the velocity of the air through the arc do not affect the yield within the experimental range studied. When the velocity is high enough to render the arc unstable the yield decreases appreciably. At very low velocities it is to be expected that the yield would decrease. Cramp and Hoyle[4] in an exhaustive study of the arc found that increasing the velocity of air through the arc increased the yield of nitrogen peroxide per *ampere* up to a maximum and then decreased it. It is important to point out, however, that their results were not on the basis of yield per given energy input, but on the basis of yield for a given current.

Haber and Platou[5] found that increasing the velocity of air from approximately 0.5 liter per minute to 2 liters per minute increased the yield of nitric acid about one-third.

Interrupting the arc so as to sweep out the gases from an extinguished arc does not give increased yields. This fact shows that after the current is shut off the kinetic energy of the molecules is not decreased instantaneously to a condition (temperature) at which the nitric oxide is stable.

Spark discharges give less nitrogen peroxide per kilowatt-hour than arcs. The use of condensers is disadvantageous.

No increase in yield results from previously ozonizing the air.

Pure nitrogen peroxide may be readily obtained from air on a small scale with the use of silica gel in connection with an electric arc.

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[4] *J. Inst. Elec. Eng.*, **43**, 319 (1909).

[5] *Z. Elektrochem.*, **16**, 802 (1910).

Determination of Nitrate Nitrogen[1]

In the Presence of Cyanamide and Some of Its Derivatives

By **Kenneth D. Jacob**

Fixed Nitrogen Research Laboratory, Washington, D. C.

Cyanamide and certain of its derivatives interfere in the determination of nitrates by reduction with Devarda's alloy.

Cyanamide, dicyanodiamide, and guanylurea are quantitatively removed by precipitation with silver sulfate. Urea, if present, is converted into ammonia by the action of urease and the nitrogen contained in the urease extract removed with silver sulfate.

After elimination of the interfering compounds the nitrate is determined by the Devarda alloy method.

These analytical methods were used at this laboratory in connection with a series of soil nitrification studies on cyanamide, dicyanodiamide, guanylurea, and urea, and have given entirely consistent and satisfactory results on several hundred separate analyses.

IN CONNECTION with investigations on the rate of nitrification of commercial calcium cyanamide[2] and some of its derivatives in the soil an accurate method for the determination of nitrate nitrogen in the presence of these compounds is desired. Of the numerous methods proposed for the estimation of nitrate nitrogen, alone or in the presence of other forms of nitrogen, those based upon colorimetric or reduction procedures have as a rule proved the most satisfactory. Colorimetric methods give accurate results when the quantity of nitrate present is comparatively small, their relative accuracy decreasing as the amount of nitrate increases. It is also often difficult to obtain a colorless solution of the nitrate, especially with soils containing considerable organic matter and soluble salts. Of the reduction methods that using Devarda's alloy in dilute sodium hydroxide solution has under ordinary conditions given consistent and accurate results in the hands of different investigators, as shown by the excellent work of Allen[3] and of Davisson.[4] While the method gives satisfactory results in the presence of considerable soil organic matter, it is unreliable in the presence of cyanamide and many of its transformation products. Modifications of the Allen method which eliminate these interfering substances are here presented.

Preliminary experiments on the recovery of added nitrate nitrogen from mixtures containing cyanamide, urea, dicyanodiamide, or guanylurea sulfate, by reduction with Devarda's alloy, gave in all cases results that were from 10 to 20 per cent above the theoretical. This fact had previously been observed by Cowie[5] in the course of nitrification experiments with cyanamide and dicyanodiamide. The high results for nitrates, in the presence of cyanamide and its derivatives, are due to the gradual decomposition of the latter compounds in hot alkaline solution with a slow evolution of ammonia, part of which appears as nitrate in the final analysis. In order to obtain accurate results the interfering nitrogen must be removed before proceeding with the nitrate determination.

For the removal of cyanamide, dicyanodiamide, and guanylurea, an adaptation of Caro's method, as improved by Brioux,[6] for the determination of combined cyanamide and dicyanodiamide was used. Brioux's method involves the precipitation of these compounds from a water solution with silver nitrate and potassium hydroxide. This procedure suggested a means of freeing the solution of cyanamide and dicyanodiamide, but silver nitrate could not be used as a precipitant because it introduced additional nitrate nitrogen. By using 100 cc. of a saturated solution of silver sulfate (containing about 0.75 gram Ag_2SO_4) the interfering nitrogen from a solution containing as much as 50 mg. of cyanamide, dicyanodiamide, or guanylurea sulfate is satisfactorily removed. The interference due to the presence of urea is also reduced, but is not completely removed by this procedure.

Urea may be completely hydrolyzed[7] to ammonia and

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[1] Received June 18, 1923.

[2] Hereafter referred to as cyanamide.

[3] This Journal, **7**, 521 (1915).

[4] *Ibid.*, **10**, 600 (1918).

[5] *J. Agr. Sci.*, **9**, 113 (1919).

[6] *Ann. sci. agron.*, **27**, Pt. 1, 241 (1910).

[7] Fox and Geldard, This Journal, **15**, 743 (1923).

carbon dioxide within a very short time by the action of the enzyme urease present in jack-bean flour. This procedure is effective in removing the interfering urea, since the ammonia formed can be easily removed by distillation before determining the nitrate. However, the extract of jack-bean flour itself contains nitrogen compounds which, on boiling with dilute sodium hydroxide, slowly evolve ammonia. The extract from 170 mg. of jack-bean flour, analyzed for nitrate nitrogen by Allen's[3] method, showed 0.39 mg. of nitrogen appearing as ammonia and 0.62 mg. as nitrate. The interfering nitrogen from the jack-bean flour extract is almost completely removed by precipitation with silver sulfate and potassium hydroxide, as shown later.

Analytical Methods

1. Nitrate Nitrogen in Absence of Interfering Compounds—This method is essentially that devised by Allen. A suitable aliquot of the solution containing the nitrate is measured into an 800-cc. Kjeldahl flask, 5 cc. of 20 per cent sodium hydroxide are added, and the total volume is made up to 350 cc. The flask is connected to a distilling apparatus, fitted with an efficient type of scrubber bulb, and boiled until 300 cc. of distillate collect in the receiver. This removes all ammonia, either free or combined. To the 50 cc. of solution remaining in the flask are added 200 cc. of water and 1.5 to 2 grams of nitrogen-free Devarda's alloy (about 60 mesh). The flask is immediately connected with the distilling apparatus, and 200 cc. are distilled into a known quantity of 0.1 or 0.05 *N* sulfuric acid, in the course of about 1 hour. The nitrogen, as ammonia, found by titrating the excess sulfuric acid with 0.05 *N* sodium hydroxide, using methyl red as an indicator, represents the nitrate present in the original aliquot.

The Kjeldahl flasks should be free from all traces of Devarda's alloy or zinc before distilling off the original ammonia; otherwise some of the nitrate may be reduced and thus fail to appear in the final nitrate determination.

2. Modification for Nitrate Nitrogen in Presence of Cyanamide, Dicyanodiamide, and Guanylurea—To a measured sample containing these forms of nitrogen are added 100 cc. of a saturated solution of silver sulfate and 10 cc. of a 15 per cent solution of potassium hydroxide. The precipitate is allowed to stand for about 1 hour, with frequent stirring, and is then filtered directly into an 800-cc. Kjeldahl flask. The precipitate is washed six times with 10-cc. portions of water, 5 cc. of 20 per cent sodium hydroxide are added to the flask, and the total volume is made up to about 350 cc. After distilling off the ammonia the nitrate nitrogen is determined as in the preceding method. Urea is only partly removed by this procedure.

Blank determinations should be run on all samples of silver sulfate, as this compound, unless especially purified, usually contains an appreciable quantity of nitrate.

3. Modification for Nitrate Nitrogen in Presence of Urea—A neutral aliquot of the original solution containing urea, nitrate, and other forms of nitrogen is treated with 10 cc. of a neutral 2 per cent extract of jack-bean flour and allowed to stand for 1 hour. At the end of this time the enzyme urease will have converted the urea present into carbon dioxide and ammonia. In order to free the solution of the nitrogen added in the jack-bean extract, it is treated with silver sulfate and potassium hydroxide solutions as in the previous procedure, and the nitrate nitrogen is determined as usual, after first distilling off the ammonia. Cyanamide, dicyanodiamide, and guanylurea are also removed by this procedure.

Experimental Results

In obtaining the data the distillations were carried out on an ordinary Kjeldahl rack, using the scrubber distilling bulb described by Davisson,[8] the bulb, condenser tube, and adapter being made of Pyrex glass and thus eliminating danger of alkali from the glass parts.

All the results have been corrected for the blank on reagents, and, in the case of soil extracts, the nitrate nitrogen present in the soil. The soil used was a Susquehanna loam that had been under cultivation as a garden for about 15 years, and contained a comparatively large quantity of organic nitrogen.

In order to determine to what extent cyanamide, dicyanodiamide, urea, and guanylurea interfere in the usual method for determining nitrates by reduction with Devarda's alloy, two sets of analyses were made, one using these compounds in water solution, and the other in the presence of soil extract. In the first case, quantities of the nitrogen compounds, each equivalent to 20.88 mg. of nitrogen, were weighed into separate Kjeldahl flasks, 350 cc. of distilled water added, and the usual nitrate determination was carried out. For the analyses in the presence of soil extract, quantities of the compounds, each equivalent to 20.88 mg. of nitrogen, were mixed with separate portions of 100 grams of air-dried soil and each sample was immediately extracted with 500 cc. of water. Aliquots equivalent to 8.35 mg. of added nitrogen were analyzed for nitrates by the procedure applicable in the absence of interfering compounds.

Table I—Interference of Cyanamide, Dicyanodiamide, Urea, and Guanylurea in Determination of Nitrate Nitrogen by Reduction with Devarda's Alloy

Nitrogen Compound	Added Organic Nitrogen Appearing as Nitrate Nitrogen			
	A[a]		*B*[b]	
	Mg.	Per cent	Mg.	Per cent
Cyanamide	4.39	21.02	1.86	22.27
	4.23	20.26	1.51	18.08
Dicyanodiamide	3.76	18.01	1.42	17.00
	3.51	16.81	1.51	18.08
Urea	2.23	10.68	0.64	7.66
	2.15	10.29	0.65	7.78
Guanylurea sulfate	3.01	14.41	0.38	4.55
	2.90	13.88	0.38	4.55

[a] In pure solution. Added organic nitrogen = 20.88 mg.
[b] In the presence of soil extract. Added organic nitrogen = 8.35 mg.

Although the results given in Table I are not entirely comparable because of the varying quantities of organic compounds used in the two cases, they show that, even in the presence of comparatively small quantities of cyanamide and some of its derivatives, an appreciable portion of the organic nitrogen appears in the final analysis as nitrate.

In order to determine the efficiency of the method for the removal of interfering nitrogen due to the presence of cyanamide, dicyanodiamide, and guanylurea, quantities of these compounds, each equivalent to 20.88 mg. of nitrogen, were thoroughly mixed with 100-gram portions of air-dried soil, and the whole was immediately extracted with 500 cc. of water. Aliquots equivalent to 8.35 mg. of added nitrogen were treated as described under (2) of "Analytical Methods," with the following results:

The interfering cyanamide, dicyanodiamide, and guanylurea nitrogen can be removed practically to within the limits of experimental error by precipitation with silver sulfate and potassium hydroxide. The interference caused by the presence of urea is reduced by this procedure, but its removal is not complete.

In order to determine the efficiency of the method for the removal of interfering urea nitrogen, soil extracts containing urea were prepared in the same manner as those used in obtaining the results given in Table II. Aliquots equivalent to 8.35 mg. of urea nitrogen were analyzed by the method previously described for the removal of urea nitrogen.

The average results given in Tables II and III compare very favorably with respect to the removal of the added forms

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[8] This Journal, 11, 465 (1919).

TABLE II—EFFICIENCY OF METHOD FOR REMOVAL OF CYANAMIDE, DICYANODIAMIDE, AND GUANYLUREA

(Added organic nitrogen = 8.35 Mg.)

NITROGEN COMPOUND		Added Organic Nitrogen Appearing as Nitrate Nitrogen Mg.	Per cent
Cyanamide		0.031	0.37
		0.023	0.27
		0.057	0.68
		0.031	0.37
	Av.	0.035	0.42
Dicyanodiamide		0.023	0.27
		0.031	0.37
		0.031	0.37
		0.040	0.47
	Av.	0.031	0.37
Guanylurea sulfate		0.065	0.78
		0.098	1.17
		0.040	0.47
		0.048	0.57
	Av.	0.063	0.75
Urea		0.452	5.41
		0.528	6.32
	Av.	0.490	5.86

of organic nitrogen. In order to determine the efficiency of the procedures as regards the recovery of added nitrate nitrogen in the presence of the organic nitrogen compounds, soil extracts were prepared in the same manner as those previously used. Aliquots containing 3.89 mg. of added nitrate nitrogen in the form of potassium nitrate and 8.35 mg. of added organic nitrogen were analyzed by one of the procedures dependent upon the nature of the organic nitrogen present.

TABLE III—EFFICIENCY OF METHOD FOR REMOVAL OF INTERFERING UREA NITROGEN

(Added urea nitrogen = 8.35 mg.)

	Added Urea Nitrogen Appearing as Nitrate Nitrogen Mg.	Per cent
	0.092	1.10
	0.045	0.53
	0.019	0.22
	0.019	0.22
	0.027	0.33
Av.	0.040	0.48

TABLE IV—RECOVERY OF NITRATE NITROGEN IN PRESENCE OF CYANAMIDE AND SOME OF ITS DERIVATIVES

(Added nitrate nitrogen = 3.89 mg., added organic nitrogen = 8.35 mg.)

ORGANIC NITROGEN COMPOUND		Added Nitrate Nitrogen Recovered Mg.	Per cent
None		3.930	101.03
		3.920	100.77
	Av.	3.925	100.90
Cyanamide		3.894	100.10
		3.928	100.97
		3.955	101.67
		3.898	100.21
	Av.	3.919	100.74
Dicyanodiamide		3.932	101.08
		3.974	102.16
		3.879	99.71
		3.960	101.80
	Av.	3.936	101.19
Guanylurea sulfate		3.896	100.16
		3.852	99.02
	Av.	3.874	99.59
Urea		3.886	99.89
		3.877	99.66
		3.919	100.74
	Av.	3.894	100.10

Colloidal Copper Hydroxide as a Fungicide[1]

By **Henry D. Hooker, Jr.**

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AT PRESENT there is no entirely satisfactory fungicide available. The two most important ones are Bordeaux and lime-sulfur, but both burn the foliage under certain climatic conditions, and neither is remarkable for its sticking or spreading properties. Bordeaux is difficult to prepare correctly and the ready-made mixtures on the market have not proved ideal. Lime-sulfur does not control some fungus diseases, such as apple blotch, and consequently fruit-growers must supplement lime-sulfur spraying by subsequent applications of Bordeaux where this disease is prevalent. Lime-sulfur is, moreover, a most disagreeable material to handle.

It was thought that a colloidal copper compound would prove an ideal fungicide. If a material having a positive electrical charge could be prepared, it should have in colloidal suspension the sticking and spreading qualities of lead arsenate. It was thought that the burning properties of Bordeaux might be eliminated by preparing an insoluble compound such as copper hydroxide in colloidal suspension because plant membranes are impermeable to colloids.

PREPARATION OF COPPER HYDROXIDE

Colloidal copper hydroxide was prepared by using a modification of the method reported by Bradfield[2] for the preparation of colloidal iron hydroxide, aluminium hydroxide, and silicic acid. A 10 per cent solution of sodium hydroxide was added to a solution of copper sulfate with constant stirring until the supernatant liquid lost its color. Copper hydroxide was thrown down as a pale blue precipitate. An excess of alkali leads to the formation of a deep blue precipitate which changes on standing to black copper oxide. This must be avoided and it is better to leave some copper sulfate in solution than to attempt to reach an end point. The mixture so prepared contains sodium sulfate, a small amount of copper sulfate in solution, and a precipitate of insoluble copper hydroxide which holds, probably by adsorption, a considerable amount of copper sulfate. The preparation of colloidal copper hydroxide depends on the removal of the electrolytes—namely, the copper sulfate and sodium sulfate in solution and likewise a large part of the adsorbed copper sulfate. This was accomplished by agitation and repeated washing by sedimentation. Distilled water was used.

When first thrown down by the addition of sodium hydroxide solution, a mixture was obtained that was far from homogeneous. This was pumped under pressure with a hand pump through a spray nozzle from one receptacle to another, to break up the precipitate and render the mixture as homogeneous as possible. This procedure was repeated after every few washings. The mixture was transferred to a tall glass vessel and allowed to settle for 24 hours. The supernatant liquid was siphoned off, distilled water was added, and the whole was mixed thoroughly by vigorous stirring. After a dozen such washings by sedimentation practically all the free salt was removed. As long as the copper hydroxide was washed in relatively small volumes of water—50 parts of water by weight to one of copper hydroxide—the supernatant liquid remained clear. After the free salt had been removed, the volume of wash water was increased to 200 parts of water by weight to 1 part of copper hydroxide, and the process of washing by sedimentation continued. After several washings the precipitate settled, leaving an opalescent, supernatant liquid. This contained a very small amount of copper hydroxide, which settled out after standing for

[1] Received July 23, 1923.

[2] *J. Am. Chem. Soc.*, **44**, 965 (1922).

several days. As the washing was continued the amount of copper hydroxide remaining in suspension after the settling of the larger particles increased until what might be termed an incipiently colloidal solution was obtained which contained 1 part by weight of copper hydroxide in 1000 of water. At this concentration and dispersion the solution foamed readily on shaking. This was the maximum concentration and dispersion obtained by the process described. The material so prepared is a delicate robin's-egg blue by reflected light and blue-green by transmitted light. The copper hydroxide remained in suspension for several weeks, but the solution became stratified.

By centrifuging in a supercentrifuge the copper hydroxide is thrown out. This may be ground up with small amounts of water, resuspended, and shaken according to the Bradfield procedure. After centrifuging a few times a true colloidal solution can be prepared.

Various modifications of this method might be suggested. It would undoubtedly require fewer washings to prepare colloidal copper hydroxide from a monovalent salt such as copper chloride. Several devices might be used to remove larger percentages of water from the copper hydroxide than is possible by sedimentation, thus making each washing more thorough. The addition of small amounts of acetic acid will peptize the copper hydroxide. The object of this work, however, was to prepare colloidal copper hydroxide from the cheapest materials by the simplest procedure. If a supply of soft water had been available, this would have been used instead of distilled water, thus reducing still further the cost of manufacture.

Spraying Experiments

Two distinct types of copper hydroxide were used in the spraying experiments. One was a sediment from which all free soluble salts had been washed, but which showed no tendency to go into colloidal suspension. When washed in a large volume of water it settled out quickly, leaving a clear supernatant liquid. The other was an incipiently colloidal preparation purified as far as possible by the sedimentation method. This material remained in suspension for a long period and foamed when shaken.

Experiments were carried out in a neglected apple orchard that had not been sprayed for several years. The materials were used in the following concentrations:

COPPER HYDROXIDE	Trees Sprayed	Concentration %	Parts by Weight of Water to 1 Part $Cu(OH)_2$	Copper Used Compared with 3:4:50 Bordeaux %
Sediment:				
1st dilution	2	0.4	250	143.0
2nd dilution	1	0.2	500	71.5
3rd dilution	2	0.1	1000	35.8
4th dilution	4	0.05	2000	17.9
Colloid:				
1st dilution	1	0.076	1315	27.0
2nd dilution	2	0.038	2630	13.5
3rd dilution	3	0.019	5260	6.8

The trees sprayed were Ben Davis. A power spray was used and the material was applied with a spray gun. The first application was a calyx spray on May 11. This was followed by sprays on May 21 and June 4. On the two latter occasions lead arsenate was added at the rate of 3 pounds of powder to 100 gallons of spray. Fifteen trees in the same orchard were sprayed at the same time with 3:4:50 Bordeaux and fifteen others with 3:100 lime-sulfur. A large number of trees were left unsprayed as checks. The only water supply available for diluting the spray material was a muddy stock pond. This water was used, though clear water would have been preferable, as mud is a negative colloid and throws copper hydroxide out of suspension.

The early part of the season was characterized by cool, wet weather, particularly favorable to Bordeaux burning. When the last spray was applied it was observed that all the apples in the trees sprayed with the copper hydroxide sediment had been burned, presumably by the first application. Contrary to expectations the first dilution of the colloidal preparation produced exceptionally severe burning; the second dilution gave burning approximately equivalent to the 3:4:50 Bordeaux; the lowest dilution produced very little burning, not much more than lime-sulfur. The first dilution of the sediment gave severe burning, though not so severe as the strongest concentration of the colloid; the second burned about equal to 3:4:50 Bordeaux; the third and fourth, slightly less. It was distinctly noteworthy that dilution of the colloidal preparation reduced burning to a greater extent than did similar dilution of the sediment.

On July 12 the fruit was removed from each of the sprayed plots and from check trees to determine the fungicidal value of the sprays. The unsprayed fruit showed both apple scab and apple blotch. Approximately 20 per cent of the fruit was diseased, 13 per cent by scab and 7 per cent by blotch. The fruit on all sprayed trees was clean, not a single sign of scab or blotch being found on any of the apples from trees sprayed with copper hydroxide. The trees treated with the first dilution of the sediment and of the colloid had lost all their apples, apparently as a result of the severe burning.

The fact which merits emphasis is that under the conditions of the experiment complete protection from both scab and blotch was afforded by the weakest concentration of the colloidal copper hydroxide used and that this spray produced very little burning, much less than 3:4:50 Bordeaux and very little more than lime-sulfur. The amount of copper used was one-fifteenth that used in 3:4:50 Bordeaux. These preliminary tests would indicate, therefore, that a great saving in the cost of fungicidal spray materials could be made by using prepared colloidal copper hydroxide. Should the results be confirmed by subsequent tests under a wide variety of climatic conditions, 1 pound of copper as colloidal copper hydroxide would suffice to spray 2 to 3 acres of apple orchard once. It is, of course, possible that an even more dilute concentration may give adequate protection and no burning.

Additional experiments on a small scale have shown that colloidal copper hydroxide can be mixed with nicotine sulfate. A colloidal solution containing 1 part of the hydroxide in 5000 parts of water was sprayed on one peach tree and on one cherry tree. This work was done with a hand pump and a rod with a disk nozzle. No evidence of burning on either kind of fruit could be found. However, no additional information concerning the fungicidal properties of copper hydroxide was obtained.

Conclusion

Preliminary experiments indicate that copper hydroxide prepared as a colloid is fungicidal to apple scab and apple blotch in concentrations of 1 part of hydroxide to 5000 of water. At this concentration it produced very slight burning. It has excellent sticking properties due to its positive charge and spreads well in dilute solution. It can be used in conjunction with lead arsenate and nicotine sulfate. Although it would be hazardous to estimate the cost of manufacture, it is clear that colloidal copper hydroxide would be much less expensive than either Bordeaux or lime-sulfur.

From Germany comes announcement of the death of **P. Friedländer**, privat-dozent for organic chemistry and technical organic technology in the Technical Hochschule at Darmstadt. Professor Friedländer is well known for his investigations on the chemistry of dyestuffs and for his work "Fortschritte der Teerfarbenfabrikation," which appeared in twelve volumes.

Studies of the Activity of Organic Nitrogenous Compounds—II[1,2]

By C. S. Robinson, O. B. Winter, and Selma Bandemer

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In a previous publication[3] it was shown that a more or less intimate relationship existed between the nitrogen present in an acid hydrolysate as amino acids and acid amides and that evolved as ammonia upon oxidation with alkaline permanganate solution as prescribed by the official methods of the A. O. A. C.[4]

In the present article the action of permanganate is further studied using two samples of protein and several of common base goods of the fertilizer trade. Previous work dealt only with the ultimate quantities of ammonia, acid amide, and amino nitrogen obtained upon decomposition. In the work herein reported an effort was made to ascertain whether or not any connection exists between the rates of decomposition of various materials and their fertilizer values. The study of the several factors influencing the results with the permanganate digestion was also undertaken.

THIS work may perhaps be characterized as an analysis of the alkaline permanganate method. In it an attempt has been made to follow the progress of the digestion and distillation by analyzing the digestion mixture at regular intervals and by collecting the distillate in fractions in each of which the ammonia was determined.

The procedure finally followed was the outgrowth of a lengthy study of the problem and of many attempts to develop a method as closely analogous as possible to the official technic. One plan tried out involved running the experiments in regular Kjeldahl flasks and sampling the contents at intervals. It was thought that satisfactory results could be obtained by assuming that the total nitrogen present in the system at any time equaled the amount originally present less the ammonia removed. Only after considerable work had been done and a number of other possibilities eliminated was it discovered that nitrogen escaped in some form other than ammonia (apparently as free nitrogen), which fact introduced appreciable errors into the results. It was found necessary actually to determine in each fraction both the ammonia in the distillate and the total nitrogen in the residue.

Apparatus

The apparatus consisted of twelve pairs of test tubes, 2.5 cm. in diameter and 25 cm. long, each tube being fitted with a perforated rubber stopper through which passed two pieces of glass tubing about 6 mm. in diameter. One of these reached almost to the bottom of the test tube and terminated in a bulb perforated with a number of holes which served to break up into small bubbles the air stream drawn through it, while the other was flush with the bottom of the stopper. One test tube in each pair served as a reaction vessel and the other as a receptacle for standard acid to catch the ammonia evolved, the outlet tube of the former connecting with the inlet tube of the latter.

Procedure

In making the determinations one-third of the amount of sample necessary to furnish 50 mg. of water-insoluble nitrogen—i. e., one-third of an official sample—was weighed into each reaction tube. The connection with the companion tube containing acid was then made and 40 cc. of an alkaline permanganate solution (one-third the official quantity) were introduced through the inlet tube, slight suction being applied to the outlet of the acid tube for the purpose. The reaction tubes were then thoroughly shaken and set in a water bath (95° C.) while the attached tubes were held outside of the bath by means of clamps.

In working with proteins it was found that complete solution was effected during the 15 minutes allowed for the temperature of the contents of the tubes to rise from that of the room to that of the bath. This procedure was arbitrarily followed with all the other materials, assuming that the alkali-soluble matter would be dissolved during this preliminary stage. Time was counted from this point and one tube removed every 5 minutes for 30 minutes, an interval corresponding to that specified for the digestion of the sample in the official A. O. A. C. methods. Each tube was removed with the acid-containing one attached and immediately cooled to room temperature to stop the reaction. The outlet of the acid-containing test tube was then attached to a suction pump to remove any ammonia remaining in the digestion mixture and the excess acid titrated as usual. The digestion residue was transferred to a volumetric flask, acidified with sulfuric acid, diluted to the mark, and used for the determination of total and amino nitrogen.

At the end of the 30 minutes, when the sixth pair of tubes had been removed, the remaining six were transferred to an oil bath. After 10 minutes one tube was taken out and another at the end of each subsequent 10-minute interval, so that the total time consumed in the experiment, exclusive of the preliminary "solution" period, was 90 minutes. The oil bath used during the last 60-minute stage was held at such a temperature (140° C.) that only a small amount of liquid remained in the last tube when it was removed. By this procedure its contents were subjected to the conditions prescribed by the official methods.

It must, of course, be admitted that this procedure, which differs markedly from that specifically fixed in the official method, may in some cases lead to very different results. The rather good agreement between the final values for the active insoluble nitrogen as determined by the two procedures indicates that such differences are but little in excess of those normally to be expected with the official method. The writers, therefore, feel confident that, in spite of the radical differences in technic, the conclusions drawn from the present work are applicable to the official procedure.

All determinations were made in duplicate and the duplicates agreed as well as could be expected.

For purposes of comparison, determinations using the same strength of alkali but omitting the permanganate were also

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[1] Received July 27, 1923.

[2] Journal Article No. 25 from the Chemical Laboratory of the Michigan Agricultural Experiment Station. Published by permission of the Director of the Experiment Station. The material contained in this article was originally to be published in two papers, the second and third in the series. As such they were read by title at the Birmingham and Pittsburgh meetings, respectively, of the American Chemical Society.

[3] This Journal, **13**, 933 (1921).

[4] Assoc. Official Agr. Chem., Methods, **1920**, p. 11.

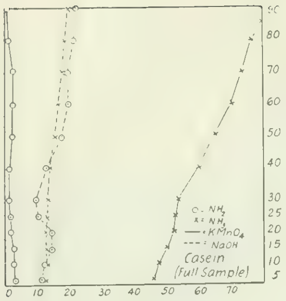

FIG. 1

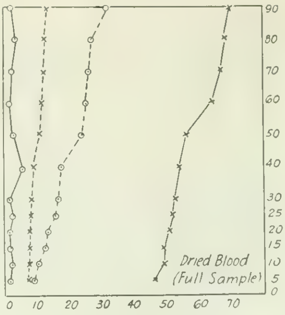

FIG. 2

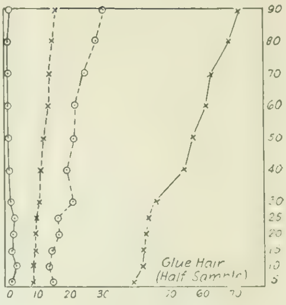

FIG. 3

made, thus making it possible to calculate the actual results due to the permanganate.

The results are shown in the accompanying figures.

EFFECT OF ALKALI ALONE AND OF ALKALINE PERMANGANATE

The chief result of the action of alkali on protein compounds is one of hydrolysis with the formation of ammonia and amino acids, the former being produced chiefly from acid amides, although there are some secondary reactions whereby some compounds other than acid amides are made to yield ammonia. While the relative amounts of ammonia and amino nitrogen produced by protein hydrolysis vary with different substances, the quantity of amino nitrogen is always much greater than the ammonia. In the most common animal proteins the ammonia formed during acid digestion amounts to about 5 to 10 per cent of the total nitrogen, while the amino fraction approximates 60 to 70 per cent. Data are not available on the alkaline hydrolysis of many materials, but these figures would be somewhat changed, the ammonia tending to increase at the expense of the amino nitrogen.

Inspection of the graphs illustrating the results of the action of alkali alone upon the materials used in the present work shows that the quantities of ammonia are unusually high, that the amino nitrogen values are low, and that their sum is usually not equal to the ammonia and amino nitrogen ordinarily found in protein. Hence it may be concluded that hydrolysis is incomplete under the conditions of these experiments. In general, both forms of nitrogen increase during the progress of the digestion and the maximum is not reached.

The permanganate graphs show an entirely different picture. Here the amino nitrogen is almost negligible in quantity and tends to decrease in amount as the digestion progresses. In the case of the full sample of glue hair where the permanganate color was discharged at the end of 20 minutes, the amino nitrogen tends to increase, the curve assuming more closely the form of that for the alkaline digestion. With the full sample of cottonseed meal the same condition exists during the middle part of the experiment, but during the last 20 minutes an increased formation of ammonia is accompanied by a decrease in the amino nitrogen. While it is apparent that some of the ammonia in all cases is produced at the expense of the amino nitrogen, the lack of agreement between the total amounts produced indicates that this is not the whole story, but that the action of the permanganate is more deep-seated, producing ammonia from linkings not ammonified by alkali alone.

ACTION OF PERMANGANATE IN RELATION TO MEASUREMENT OF NITROGEN ACTIVITY

Two fundamental criticisms of the alkaline permanganate method have been made. It has been stated that results cannot be accurately duplicated because of the terminal conditions which deal with an incomplete reaction progressing with considerable rapidity and necessitating a control of conditions not ordinarily possible. It has also been shown that with substances which decolorize the reagent the results obtained are due to quite different causes than those secured with materials which do not decolorize the permanganate solution. The writers have stated in a previous paper[3] that the former criticism was of greater theoretical than practical importance. It does, however, become significant, as was stated in a later paper,[5] in cases where, because of foaming, the duration of the digestion and distillation is protracted beyond the specified 90 minutes. The curves herewith presented substantiate these statements.

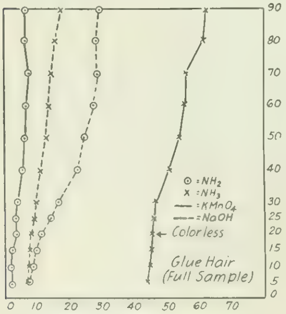

FIG 4

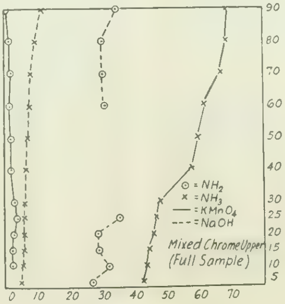

FIG 5

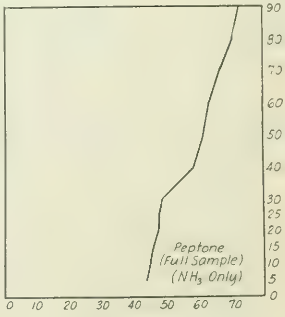

FIG 6

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[5] J. Assoc. Official Agr. Chem., 5, 448 (1922).

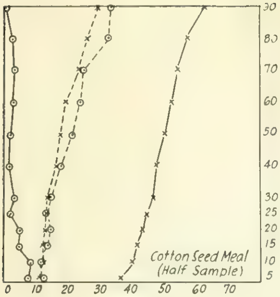

FIG 7

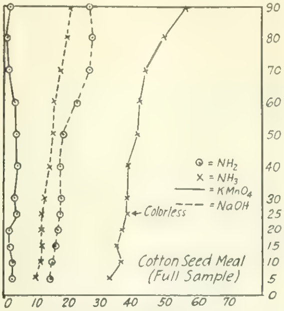

FIG 8

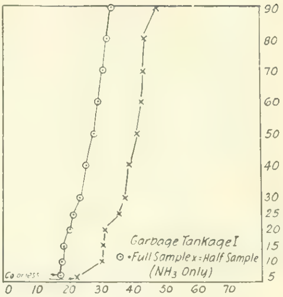

FIG. 9

The total quantity of ammonia produced, which is a measure of the activity of the materials under consideration, is the sum of two factors: (1) that formed during the preliminary digestion or "solution" period, and (2) that formed during the measured digestion and distillation periods. The former constitutes most of the ammonia in the first tube removed, while the latter is, of course, the rest of the ammonia collected in the other eleven tubes. The ammonia fraction may be further subdivided into that which is liberated by the alkali alone and that set free by the permanganate. With the exception of the "base goods" the values for the first portion vary between 5 and 12 per cent of the total nitrogen. The "base goods" showed 25 per cent ammonia in the first sample taken in the alkali digestion. This material was composed of garbage, beet slop, and leather, and had been mixed in the usual way with rock phosphate and sulfuric acid and allowed to stand in a den. The nature of the resulting product is problematical. Had the organic nitrogen been ammonified, it would, of course, have been washed out, as only the water-insoluble portion was used for this work. It is hard to conceive of a degradation product which would be so readily ammonified as this is. With this exception the initial ammonia contents show nothing of interest or importance.

The quantities of ammonia produced up to the taking of the first sample are given in Column 4 of Table I. Column 5 shows the ammonia produced during the remainder of the digestion and distillation. It is a rather interesting fact that, by bringing the temperature up to the digestion point during 15 minutes and holding it there for 5 minutes, results are obtained which, with few exceptions, have the same relative magnitudes as those obtained by the official method, which requires 90 minutes to carry out. Many analysts assume that materials having 50 per cent or more of this insoluble nitrogen in the active form are made from base goods of satisfactory quality. If a passing value of 30 per cent, instead of 50 per cent, were used, all the materials would pass by about the same margins that they do in the present official method.

TABLE I—ACTION OF PERMANGANATE ON ORGANIC NITROGENOUS COMPOUNDS

MATERIAL		(1)[a]	(2)	(3)	(4)	(5)
Casein		74.35	82.35	70.59	46.58	35.77
Dried blood		68.70	70.00	64.70	46.84	23.16
Glue hair	Full	67.45	62.25	55.78	43.93	18.32
	Half	66.66	72.00	62.35	39.94	32.06
Chrome uppers		64.35	68.47	61.10	42.18	25.29
Cottonseed meal	Full	52.60	56.95	42.30	32.27	24.68
	Half	66.08	62.10	52.18	36.50	25.60
Garbage tank	I, full	28.38	33.47	29.19	17.28	...
	I, half	45.60	47.15	42.58	22.08	...
	II, full	...	25.10	23.31	16.40	...
	II, half	...	42.86	38.80	24.91	
Tartar pomace	Full	33.79	34.24	29.76	14.43	...
	Half	42.06	46.69	38.48	26.40	...
Tobacco stem	Full	22.68	25.09	20.08	16.35	...
	Half	34.36	31.41	27.70	19.75	...
Base goods, I	Full	32.28	...	...	...	...
	Half	52.64	...	...	41.38	...

[a] (1) Active insoluble nitrogen, official method.
(2) Active insoluble nitrogen, step method.
(3) Active insoluble nitrogen, at 60 minutes.
(4) Ammonia formed during preliminary digestion plus ammonia present.
(5) Ammonia formed after preliminary digestion.

The influence of the initial ammonification is especially noticeable in the cases of the distinctly low-grade materials, garbage tankage, tartar pomace, and tobacco stems. Although both the slopes of the curves and the amounts of ammonia produced during the solution period are less than those in the high or medium grade, it is the initial ammonification factor that determines the final value. The importance of this will be taken up later.

The last column shows the ammonia liberated during the regular digestion and distillation periods less the first

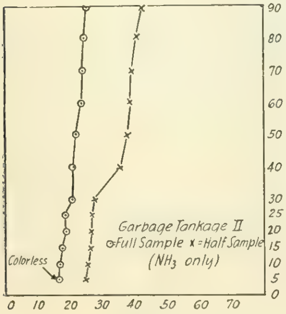

FIG. 10

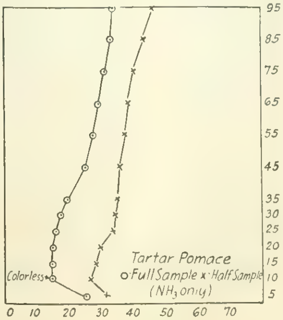

FIG. 11

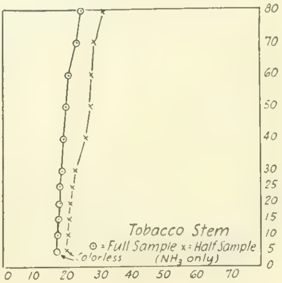

FIG. 12

5 minutes included in the first sample taken. A comparison of these values with those in the preceding column shows that by far the larger part of the ammonia is produced prior to the true digestion and distillation.

Assuming that the rate of reaction decreases, the evolution of ammonia should be rather slow by the time the distillation is completed, since the greater part is given off prior to its commencement. An inspection of the curves shows this to be true, their direction sharply approaching the vertical with the commencement of sampling. There are some differences in the rates, casein and the half sample of glue hair showing a somewhat more rapid evolution of ammonia than the others throughout the course of the reaction. The differences in the slopes of the curves at the end of the distillation indicate the importance of the criticism previously mentioned—i. e., that at the end of the process the reaction is still progressing so rapidly that accurate results are not obtainable. In the cases of casein, both samples of cottonseed meal, and to a lesser extent the half sample of glue hair, the curves still deviate from the vertical axis, indicating that ammonia is still being given off rather rapidly (from 3 to 7 per cent during the last 10 minutes); while in the other cases the curves practically coincide with the vertical axis, indicating that less than 1 per cent of the nitrogen is being converted into ammonia during the last 10 minutes. In some cases, therefore, the reaction evidently has approached completion and little care need be exercised in accurately controlling the final conditions. In others, however, this is not true.

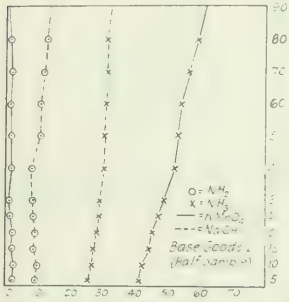

FIG 13

TABLE II—PER CENT OF ACTIVE INSOLUBLE NITROGEN AS DETERMINED BY THE OFFICIAL AND MODIFIED METHODS

Sample	Official Method	Modified Method	Sample	Official Method	Modified Method
1	1.08	1.05	144	1.26	1.31
146	0.42	0.47	148	0.46	0.46
150	0.20	0.21	153	0.54	0.61
162	0.51	0.53	169	0.42	0.39
172	0.30	0.33	182	0.22	0.23
208	0.93	1.02	388	0.11	0.12
389	0.18	0.19	396	0.42	0.44
404	0.30	0.32	412	0.38	0.40
415	0.13	0.14	417	0.81	0.77
419	0.22	0.23	420	0.19	0.19
425	0.20	0.20	455	0.62	0.64
465	0.48	0.55	476	0.61	0.64
478	0.23	0.24	480	0.35	0.37
481	0.36	0.37	483	0.27	0.29
487	0.14	0.16	495	0.40	0.42
500	0.43	0.45	501	0.67	0.69
502	0.28	0.29	505	0.18	0.20
508	0.17	0.17	512	0.40	0.43
515	0.52	0.45	523	0.39	0.42
712	0.17	0.18	716	0.57	0.58
717	0.19	0.20	721A	0.24	0.22
721B	0.41	0.42	723	0.19	0.19
725	0.28	0.29	726	0.13	0.14
728	0.49	0.48	730	0.48	0.49
731	0.31	0.30	24860	3.42	3.18
24862	3.46	3.42	5–22–1	0.47	0.47
15	3.30	3.38	11	2.93	2.82
3577	1.23	1.24	2–1–2	0.52	0.56
2–12–2	0.93	0.93	3–10–4	1.38	1.36
4–8–8	2.36	2.25	1–5–10	0.18	0.21
18	0.51	0.60	5–21–15	3.90	4.45
2–21–46	3.94	4.02	4213	0.28	0.29
6–21–2	3.06	3.41	11–21–1	4.52	5.10
11–21–7	2.19	2.13	11–21–8	0.47	0.52
Peat I	1.07	1.11	Peat II	0.62	0.65
Peat III	0.85	0.76	2–1–2	0.57	0.60
1–8–5	0.79	0.82	....	..	..

Most of the curves reflect the increase in temperature with the commencement of the distillation, but are fairly straight above and below this point. The most noticeable exception is the sharp break in the curve for the full sample of cottonseed meal, due probably to the increase in the concentration of the reagents during the last 20 minutes of the distillation.

To the second factor—viz., a deficiency in permanganate—Jones[6] ascribed the anomalous results with cottonseed meal. He also showed that the admixtures of reducing substances with dried blood lowered the activity of this material as estimated by the alkaline permanganate method. This is corroborated by the authors' work. Fig. 2 shows the result of mixing starch with dried blood. These curves were obtained as follows: Dried blood and starch were mixed in such proportions that the dried blood composed 100, 80, 60, 40, and 20 per cent of the mixture. These materials were then handled in the usual manner, the samples being weighed out on the basis of the insoluble nitrogen content. Increasing proportions of starch cause corresponding decreases in the activity of the dried blood until the amount of nitrogen ammonified is reduced from 60 to 20 per cent.[7]

Attention has been called to the fact that most of the ammonia is produced during the early stage of the digestion, and it has been pointed out that the sequence of materials when arranged in order of the percentages of nitrogen ammonified is the same whether based on the ammonia formed during the first 20 minutes or on the whole period of reaction. This suggested the possibility of modifying the present alkaline method so as to reduce the time and attention required. In previous attempts to accomplish this, stress was laid on the relative amounts of sample and reagent in trying to remedy the above-mentioned defects in the method. The following suggested modification does not do this. The results by it are no more reliable than those obtained by the official procedure and whatever can be said in this respect for or against the one can be likewise said of the other. However, the results by the modified method appear to be just as valuable as those with the present official method, and they are obtained with considerable economy of time and trouble. After several trials the following procedure has been selected as giving results comparable to those obtained by the official method:

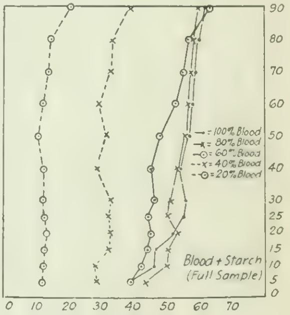

FIG. 14

> A sample containing 50 mg. water-soluble nitrogen as determined by the official method is weighed into a 500-cc. Kjeldahl flask, the prescribed amount of alkaline permanganate solution added, and the flask connected with a condenser. A small flame under the flask is regulated so that about 100 cc. of distillate passes over in 45 min. The distillate is caught in standard acid and at the end of this time the excess is titrated. If the solution tends to foam a few drops of octyl alcohol may be added.

By this procedure the actual time involved is reduced to one-half of that demanded by the present official method. The attention required is also reduced since the process is a continuous one and not divided into two parts. This method has been compared with the official one on seventy-three different materials. The results by the two methods check as well as do duplicates by the official method. (Table II)

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[6] Annual Report, Vermont Agr. Expt. Sta., **1899**, p. 139.

[7] Work done by A. W. Lowell.

Determination of Total Sulfur in Soils and Silicate Rocks[1]

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A rapid and efficient method is offered for the determination of total sulfur in large charges of soils by fusion at a relatively low temperature and without use of platinum. Complete oxidation and absolute disintegration is assured. Aqueous extraction and filtration of the melt insures removal of aluminium, iron, manganese, and alkali earths, and eliminates any interference of native barium which vitiates results obtained by the generally followed hydrochloric acid extraction. Necessity for silica dehydration is obviated and a minimum of potassium salts is insured.

The determination of sulfates involves a number of chemical considerations which have been studied in particular by Allen and Johnston,[1,*] Blumenthal and Guernsey,[3] and Hirst and Greaves.[8]

Much difficulty has been encountered in making speedy and accurate determinations of total sulfur in soils. At its 1919 meeting the Association of Official Agricultural Chemists directed the junior author, as Referee for Soils, to study the problem. In connection with that study,[10,11,12] the present mode of procedure was developed.

Most soils are of low sulfur content and large charges are necessary to insure sufficient analytical quantities of barium sulfate. Assurance of complete combustion and absolute disintegration of the mass must be had. When these two requirements are met there is the further difficulty of insuring complete removal of the oxidized sulfur from the insoluble residue. In studying methods the authors endeavored to secure complete oxidation and removal of sulfates from the insoluble siliceous residue by boiling with concentrated nitric acid and filtering through a 10-cm. Büchner, the use of which facilitated washing of a thin layer of soil. No assurance was obtained that complete oxidation of native sulfur materials was effected. It was also found by the authors and their collaborators[12] that with longer periods of boiling of soil with nitric acid and subsequent replacement of nitric acid by hydrochloric acid, lower sulfate recoveries were obtained. It appeared that this inverse relationship of time to recovery was due, in part at least, to the interference of *barium*. The common occurrence of barium in soils was shown by Failyer.[4] It is obvious that this element will be dissolved by hydrochloric acid extractions of the melts secured by the several fusion methods.

The presence of iron and aluminium in hydrochloric acid solution has been considered detrimental to the accuracy of barium sulfate determinations. Williams[19] showed that sulfate determinations in soils were consistently higher if the iron was removed by ammoniacal precipitation. It is not clear, however, whether the higher results obtained from the ammoniacal eliminations by Williams are due to (*a*) prevention of the solvent action of ferric and aluminium chloride, (*b*) obviating the loss of sulfate from a double iron barium sulfate—a point advanced also by Talbot,[17] or (*c*) to sulfate impurities in the ammonia. No mention was made by Williams of blanks upon ammonia. The writers have found that the amount of ammonia used must be definite and corrected for, even with the best high-grade chemical. MacIntire and Shaw[12] have further pointed out that precipitation of barium sulfate from solutions of equal ferric chloride content is influenced by concentration and by temperature. It was shown further that, after applying empirical blanks, three ammoniacal precipitations are necessary to prevent occlusion of sulfate in the hydrated ferric oxide.

Hart and Peterson[6] compared the official (Hilgard), modified Van Bemmelen aqua regia, and Osborne sodium peroxide methods. They concluded that the latter was superior, even without elimination of ferric and aluminium chlorides and silica from solution prior to precipitation of barium sulfate. The Osborne[14] method, applied to soils, calls for the solution of the sodium hydroxide-peroxide melt with hydrochloric acid, and addition of an indefinite amount of ammonia to neutrality. The original Fraps[5] method using potassium nitrate ignition after a preliminary digestion with nitric acid, and its subsequent modification[9] calling for calcium nitrate instead of potassium nitrate when applied to soils, both called for hydrochloric acid solution of ignited residue. Hart and Peterson[6] made a hydrochloric acid solution of the peroxide melt without elimination of iron and at a volume sufficient to inhibit precipitation of silica. Shedd[15] also obtained a strong hydrochloric acid solution of the peroxide melt, leaving iron and silica in the solution and guarding against inclusion of silica in the barium sulfate by hydrofluoric plus sulfuric acid ignition. In the A. O. A. C. official method[2] the 1-gram soil-charge fusion with 5 grams of sodium carbonate is extracted with hydrochloric acid and made to volume, 0.2 or 0.4-gram equivalent aliquots being used for the determination of barium sulfate. In using magnesium nitrate to effect oxidation, Swanson and Latshaw[16] made a hydrochloric acid solution of the pulverized, ignited residue.

In all the foregoing it will be observed that the melt was dissolved in hydrochloric acid. This the authors believe to be a serious disadvantage, if not an error, for several reasons: first, the excess of acid necessary to effect solution is stronger than permissible for the precipitation of barium sulfate; secondly, native barium and strontium present as carbonates are dissolved and during the prescribed digestion some barium sulfate is occluded in the acid-insoluble portion of the melt; thirdly, the interfering elements iron, aluminium, and possibly manganese are dissolved; and fourthly, the alkali and alkali-earth silicates are dissolved and maximum silica content is carried by the hydrochloric acid solution. In the procedure advanced by the writers, the melt is disintegrated by aqueous digestion and filtered before acidifying. By this process all iron, barium, and some aluminium are retained as silicates or carbonates in the water-insoluble residue, while much of the silica is eliminated as silicates.

In only the Hillebrand[7] method, where potassium nitrate is used, does it appear that the melt is dissolved in water and filtered from alkaline solution. Practically the identical technic used by Hillebrand has been advanced recently by Thomas,[18] and by Mahin and Carr.[13] In the present method the minimum of undesirable potassium salts is insured and the advantageous features of several different procedures have been incorporated.

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[1] Received August 20, 1923.

[*] Numbers in text refer to bibliography at end of article.

PROCEDURE

The instructions and notes sent out to A. O. A. C. collaborators are here given.

PREPARATION OF MIXTURE—Place a 5 to 10-gram charge of 0.5-mm. fineness into a 100-cc. nickel crucible; add equal weight of C. P. anhydrous sodium carbonate, and mix well with a stout nickel stirring rod of such length as to permit introduction into the furnace to be used in the fusion. Pipet carefully 4 cc. of water into each 10 grams of soil; stir well to a stiff paste, adding more water if necessary, a few drops at a time. Immediately add successive portions of about 1 gram of sulfur-free sodium peroxide, stirring well after each addition to obviate excessive frothing and overflow. Continue to add peroxide until the mixture becomes dry and granular, and then add, as a surface coating, enough to make the total peroxide addition 25 grams per each 10 grams of soil. Place the mixture in an electric furnace.

FUSION OF MIXTURE—Maintain a temperature of between 400° and 500° C. during the first half hour, then raise the temperature rapidly to bright red heat (about 900° C.) and continue the fusion at this temperature for about 10 minutes. Withdraw the crucible from the muffle quickly, manipulate so as to cause the melt to spread out in a thin sheet over the interior of the crucible, and cool rapidly by contact with some good conductor in cool atmosphere.

DISINTEGRATION OF MELT—Place the chilled crucible sideways in 600-cc. beaker; immerse in distilled water. Add about 5 cc. of ethyl alcohol to decompose sodium manganate. Cover beaker with watch glass, place on a cold electric hot plate, and apply heat. Boil briskly until all the melt is disintegrated (30 minutes are ordinarily sufficient). When the suspension has assumed a flesh-colored, flocculent appearance, with no glassy green lumps of the melt in the interior of the crucible, remove the crucible and rod from the beaker and wash any flaky particles back into beaker with the aid of a policeman, rinsing several times with hot water. (Should small glassy particles still cling to the inside of the crucible, disintegrate by boiling water in the crucible over the hot plate or a small flame and add crucible content to main volume.) Filter immediately by suction through a 9-cm. Büchner—a liter beaker placed under a bell jar being the most convenient arrangement.

FILTRATION AND WASHING—When no more of the liquid can be drawn through the filter, return residue together with the filter paper to the original beaker, washing any adhering particles carefully from the funnel. Add about 1 gram of sodium carbonate, macerate with the stirring rod, add 75 to 100 cc. of water, and bring to a brisk boil while *stirring vigorously*. Again throw on to a Büchner filter, suck nearly dry and wash three or four times, with about 20 cc. of hot water, to a volume of 500 cc., or 700 cc., for the 5 and 10-gram charges, respectively.

ACIDULATION OF FILTRATE AND DEHYDRATION OF SILICA—Cover the beaker containing the filtrate with a watch glass and (*important*) place a supported funnel with its stem bent so it just reaches into the lip of the beaker. Through the funnel pour gradually about 80 cc. of concentrated hydrochloric acid per each 10-gram charge of soil, taking care that the acid runs down the side of the beaker. Slightly lift the cover glass and gently stir with a stirring rod, watching for strong effervescence. If effervescence does not ensue, add more acid *immediately* until effervescence occurs. *If the filtrate remains clear* when concentrated to a volume of 400 cc., the barium sulfate precipitation may be effected immediately by the addition of barium chloride solution, with the silica remaining in solution.[7] However, to cover all cases, proceed as follows: Transfer acidulated filtrate to a shallow porcelain evaporating dish of 1000-cc. capacity as soon as effervescence has ceased. Place the dish 1 to 2 inches above an electric hot plate at full heat. When crystallization begins, raise the dish about 3 inches from the hot plate. Permit evaporation and dehydrate without stirring, breaking the surface crust occasionally to expedite evaporation.

PRECIPITATION OF BARIUM SULFATE—To the dehydrated mass add 0.5 cc. hydrochloric acid and 200 cc. water. Dissolve the salts completely by warming. Filter off the silica on a Hirsch funnel using No. 2 Whatman filter, or paper of equivalent texture. Wash six times with hot water to a volume of about 400 cc. Heat the filtrate, add slowly 10 cc. of 5 per cent barium chloride solution, and allow to stand over night. Filter barium sulfate on a Gooch asbestos filter, ignite in an electric furnace (or place Gooch in a porcelain crucible over a burner flame), cool, and weigh.

NOTES AND SUGGESTIONS

FUSION MIXTURE—Sodium carbonate serves both to moderate the speed of the oxidative process and to eliminate barium as barium carbonate in the first extraction. Optimum proportions of charge and sodium carbonate have been determined empirically by means of charges of pure quartz. The addition of sodium peroxide should be so regulated as to permit the comfortable handling of the crucible with the fingers, which will obviate excessive frothing and loss from overflow. Time is conserved by the simultaneous mixing of a number of charges. Should solidification of the mixture occur at any time during the mixing process, it may be reverted to the pasty consistency by immersion of crucible into hot water for a few minutes.

FUSION OF MIXTURE—Speed is insured by the use of a large electric furnace, but any sulfur-free heat may be utilized. It is important that the specified temperature be not exceeded until the preliminary oxidation process has been insured, after which complete disintegration should be effected at a higher temperature. The formation of a thin layer of the melt and its rapid crystallization on the interior of the crucible are essential to maximum efficiency.

DISINTEGRATION OF MELT—The melt is usually completely disintegrated by the procedure outlined. Aqueous digestion over night offers no advantage. Furthermore, the successful use of the hot plate is conditioned upon the fact that the disintegration is started with a clear liquid in the beaker and with all the melt contained in the crucible. The presence of suspended material in the beaker at the beginning will make the use of the hot plate impossible on account of severe bumping, and a steam bath or water bath will have to be employed with a consequent delay of 2 or 3 hours in the process. The disintegration is completed by the action of the boiling water alone without any other mechanical agitation.

FILTRATION AND WASHING—The filtration of the alkaline aqueous extract removes iron, manganese, a good portion of the aluminium, all the barium, and earthy bases—mostly in the form of carbonates and silicates.

ACIDULATION OF FILTRATE AND DEHYDRATION OF SILICA—The covering of the beaker and addition of acid as directed, rather than pouring in and stirring with a rod, is most important. *Often no silica precipitation takes place*, particularly if the solution is left to come to room temperature prior to addition of acid, even after subsequent concentration to a volume far below that from which the barium sulfate precipitation is made. By this procedure the dehydration process is also greatly facilitated and expedited. The silica usually comes out as coarse crystals after some sodium chloride has crystallized and the full evaporation and dehydration is accomplished in about 4 hours. The use of inverted tripods on the hot plate affords a very convenient means of adjusting the distances for the evaporation and dehydration of the silicic acid.

Barium chloride additions show no detrimental effect upon sulfate recoveries and sulfates added to the melt as barium sulfate are completely recovered.

EXPERIMENTAL

Since a perfectly clear melt is obtained by the fusion technic, it is apparent that complete disintegration of the soil

Table I—Effect of Soluble and Insoluble Sulfate Additions to Soils upon the Sulfate Recovery Obtained by the Proposed Method

Soil	Weight of Sample G.	$BaSO_4$ Equivalent of Addition as $FeSO_4$ G.	$BaSO_4$ G.	—$BaSO_4$ Determined— A G.	B G.	Average G.	Recovery of $BaSO_4$ Equivalent of Sulfate Addition Actual G.	Variation G.
Tennessee 4893	5	None	None	0.0115	0.0125	0.0120	.	....
Tennessee 4893	10	0.1851	None	0.2101	0.2085	0.2093	0.1853	0.0002
Kansas 1	5	None	None	0.0224	0.0222	0.0223		.....
Kansas 1	5	0.0755	None	0.0980	0.0992	0.0986	0.0763	0.0008
Kansas 1	5	None	0.1000	0.1217	0.1225	0.1221	0.0998	−0.0002

mass is assured. It is next essential (1) that complete removal of sulfate be secured, and (2) that barium, and possibly strontium, exert no interference in the removal of sulfates formed during the oxidative and disintegrative reactions utilized in obtaining a perfect melt. Since all barium and strontium are converted into carbonate form and a large excess of carbonate is present in the aqueous solution of the melt, those elements may be considered as eliminated as silicates along with iron and aluminium by the proposed procedure. To assure attainment of these two essentials, two soils, one from Tennessee and one from Kansas, were fortified with soluble and insoluble sulfates. The use of barium sulfate for the latter purpose provides both an insoluble sulfate and the presence of the interfering element barium. Full recoveries of both added soluble and insoluble sulfates are shown by the data of Table I, which gives the differences between the two soils before and after fortification.

The further fact that the presence of either soluble or insoluble barium in the soil before sodium carbonate–peroxide fusion is of no effect upon the recovery of sulfate, is also shown by the data of Table II.

Table II—Effect of Soluble and Insoluble Barium Additions to Soil upon Sulfate Recovery by the Proposed Method[a]

$BaSO_4$ Equivalent of Additions of Barium as $BaCl_2$ G.	$BaSO_4$ G.	—$BaSO_4$ Determined— A G	B G.	Average G.	Variation in $BaSO_4$ Equivalent Recovery as Influenced by Barium Additions[b] G.
None	None	0.0224	0.0222	0.0223	. .
0.0250	None	0.0230	0.0211	0.0221	−0.0002
None	0.1000	0.1217	0.1225	0.1221	−0.0002

[a] A 5-gram sample of Kansas 1 soil was used in each determination.

[b] $BaCl_2$ and $BaSO_4$ additions may be considered as additions of $BaCO_3$ and $BaCO_3$ plus Na_2SO_4, since the Na_2CO_3–Na_2O_2 fusion converts all barium to the carbonate form in the melt.

The removal of iron and aluminium in granular form by an aqueous extraction and filtration of the melt is very desirable. The primary consideration in mind, however, was that of elimination of the barium, for the hydrochloric acid solution of the melt brings into play the undesirable preliminary reaction of soluble barium chloride and soluble sulfate. With increased concentration of the hydrochloric acid solution of the melt this reaction between native barium and sulfur may be minimized during the preliminary digestion prior to filtration. However, if the hydrochloric acid extract is evaporated to effect removal of silica, as prescribed in most of the acid extractions of melt, still further opportunity is afforded for barium sulfate precipitation and loss along with the dehydrated silica. Or, if the barium sulfate is precipitated from a hydrochloric acid solution of the melt, without the removal of silica by dehydration, an excess of acid exerts a solvent action upon the barium sulfate formed after the addition of the barium chloride solution. Again, this excess of hydrochloric acid may not be killed off by ammonia, because of (1) the undesirability of ammonium salts, (2) the necessity for an absolute blank upon the amount of ammonia used, and (3) the necessity for sufficient excess of acid to care for the dissolved iron, aluminium, and manganese. As stated previously, the aqueous extract has additional advantages over the acid solution of the melt. The insoluble residue from the melt not only removes all barium, strontium, iron, manganese, and phosphorus pentoxide, but it leaves these elements for separate determination. In addition, it takes from solution more silica than does the acid solution.

Table III—Comparison between Aqueous and Hydrochloric Acid Solutions of Melts of Soil and Soil Fortified with Barium Chloride and Barium Sulfate

Soil[a]	$BaSO_4$ Equivalent of Barium Addition as $BaCl_2$ G.	$BaSO_4$ G.	—$BaSO_4$ Determined— Aqueous Alkaline Extraction A G.	B G	Average G.	HCl Extraction A G.	B G.	Average G.	Variation between Acid Extract and Aqueous Alkaline Extract G.
Kansas 4	None	None	0.0182	0.0200	0.0191	0.0154	0.0170	0.0162	−0.0029
Kansas 5	None	None	0.0180	0.0185	0.0183	0.0124	0.0140	0.0132	−0.0051
Kansas 6	None	None	0.0130	0.0124	0.0127	0.0107	0.0102	0.0104	−0.0023
Kansas 1	None	None	0.0224	0.0222	0.0223	....	....	...	......
Kansas 1	0.0250	None	0.0211	0.0230	0.0221	0.0140	0.0130	0.0135	−0.0086
Kansas 1	None	0.1000	0.1225	0.1217	0.1221	0.0224	0.0285	0.0254	−0.0967

[a] A 5-gram sample used.

The recoveries of sulfate by aqueous and hydrochloric acid extractions for soil and soil fortified with barium chloride and barium sulfate are shown by the data of Table III. It is apparent that the recovery of sulfate by the acid extraction is consistently lower than that obtained in the aqueous alkaline extraction. It is also apparent that a constant of sulfate and an increase in barium result in an increased discrepancy between the two methods of extraction. It is still further emphasized that, with high sulfur content, sulfate unrecovered by the acid extraction is practically equivalent to the amount added. But in the aqueous extraction of the fortified soil the recovery was equivalent to the amount of insoluble sulfate added. These data demonstrate the fallacy of hydrochloric acid extraction of soil melts; this point has not been stressed by investigators, so far as the writers are aware. The data of this table afford further proof that normal and abnormal occurrences of barium are of no effect in hindering sulfate recovery from soil melts.

Variations between 5 and 10-gram charges had no effect upon the accuracy of the method. In comparisons between these two charges it was found that the proportionate recoveries were obtained with a constant ratio of soil to sodium carbonate–peroxide. Comparisons are therefore absolute when the results from the more feasible 5-gram charges of soils of high organic matter content are compared with analyses of 10-gram charges from soils of low organic matter and sulfur content.

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Determination of Dissolved Oxygen in the Presence of Iron Salts[1]

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A review of the literature on the determination of dissolved oxygen is given. The modified Winkler method is shown to give erroneous results in the presence of iron salts. These errors cannot be corrected by applying a factor based on the amount of iron present. The Letts and Blake modification of the Levy method is found to give results which check the gasometric determinations in the presence of iron salts and organic matter.

THE determination of dissolved oxygen is undoubtedly the most frequently used and the most important of all the chemical methods available for the investigation of water pollution problems. It measures the capacity of a body of water for receiving organic matter without causing nuisance; it measures one of the important factors affecting fish life; it is one of the important steps in the biological oxygen demand test for measuring the important portion of the oxidizable substances in the sample; and it furnishes valuable information concerning the biological and biochemical reactions going on in the stream. Naturally, a determination of such importance has received considerable attention in the past—in fact, no less than thirteen distinct methods have been proposed.

To be successful, a method for determining dissolved oxygen must meet two requirements. First, on account of the small amount of substance to be determined (a few milligrams per liter), it must be exact; second, it must be carried out in compact, light apparatus capable of field operation, since the samples cannot be transported without undergoing chemical change.

Previous Work

The method least subject to chemical errors and probably the first to be proposed is that of Bunsen.[1,*] In this method the gases are boiled out either under atmospheric pressures or diminished pressures as practiced by Adeney,[2] Thresh,[3] and others.[4] The gas collected is then determined by ordinary absorption methods. It is too cumbersome for field work (although Birge[5] has designed a metal apparatus for field use) and requires considerable skill for accurate manipulation, but it is still the standard by which all new volumetric or colorimetric methods are judged.

Shutzenberger[6] made use of the absorption of oxygen by sodium hyposulfite. The determination was made in a current of hydrogen with indigo as an indicator. The hyposulfite solution was standardized against an ammoniacal copper sulfate solution. Investigators differed on the reliability of this method. It was claimed that hydrogen peroxide was formed during the titration and the results were said to be too low, with variations of 0.5 cc. from gasometric methods.

Mohr[7] made use of the oxidation of ferrous iron to ferric iron by the dissolved oxygen in an alkaline solution. To one of duplicate samples he added a solution of standard ferrous iron, made the water alkaline with ammonium hydroxide and then acid; to the other he added acid immediately, then standard ferrous solution, and titrated both with standard permanganate. The difference between the two titrations is proportional to the amount of oxygen in the water. Some investigators have declared that this method gives low results, while others say the results are too high.

Levy[8] modified Mohr's method using potassium hydroxide and a bulb with a stopcock at both ends and a funnel at one end to introduce the reagents. Letts and Blake[9] used a separatory funnel and sodium carbonate as the alkali.

Thresh's[3] method consists in the oxidation of hydriodic acid by the oxygen in the water to give free iodine. This is done in the presence of nitrites, which by forming nitric oxide furnish a carrier for the oxygen. A blank is run to correct for the nitrite added and that present in the water. The released iodine is titrated with standard thiosulfate in a current of coal gas or under a layer of petroleum. This method is accurate but too cumbersome for field use.

Direct titration of the dissolved oxygen was accomplished by Linossier.[10] He avoided precipitation of iron by the presence of sodium potassium tartrate and titrated the free oxygen with standard ferrous sulfate solution with phenolsafranine as an indicator.

A few colorimetric methods have been proposed. Ramsay[11] allowed the oxygen in the water to oxidize a cuprous salt to a cupric salt, thus going from a colorless to a blue solution. The intensity of the color was proportional to the oxygen present. He used standard tubes made from sodium chloride and copper sulfate reduced with sulfur dioxide gas as comparates. His method was never successful, since the color faded from the standards on standing, and the color of the water interfered as also did the nitrites. Mackay and Middleton[12] absorbed the oxygen from a portion with alkaline pyrogallol. They boiled another equal portion to get rid of the oxygen and after the addition of pyrogallol to the boiled sample added air until the color matched the first sample. From the amount of air added the dissolved oxygen was calculated. The method was inaccurate because the air added could not be easily measured and the apparatus required was cumbersome.

The method commonly used at present for the determination of dissolved oxygen in water is that of Winkler.[13] It depends on the oxidation of bivalent manganese (Mn^{++}) by the dissolved oxygen in an alkaline solution. The oxidized manganese oxidizes iodide in an acid solution, giving free iodine. The liberated iodine is titrated with standard sodium thiosulfate solution. This method has been found to check very well with gasometric determinations. It gives too high results in the presence of nitrites. Winkler[13] recognized this fact and proposed to correct by titrating a separate sample with a weak manganese chloride solution. This means is out of the question for field work.

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[1] Presented before the Division of Water, Sewage, and Sanitation at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[*] Numbers in the text refer to the bibliography at end of the article.

The modification now adopted by the Standard Methods of the American Public Health Association is that of Rideal and Stewart,[14] which oxidizes the nitrites and easily oxidizable matter in the water with potassium permanganate in acid solution. The excess permanganate is subsequently destroyed with sodium oxalate. Hale and Melia[15] have prevented the effect of nitrites by adding potassium acetate before titration, thus repressing the hydrogen-ion concentration and preventing the interaction of the nitrites with the hydrogen iodide.

Winkler[16] has recently proposed a method for the estimation of dissolved oxygen in the presence of much nitrate and organic matter. He oxidizes the organic matter with hypochlorite. One sample is run as a blank and another after treatment with manganese chloride, potassium hydroxide, and potassium iodide, the same as in his original method.

While a relatively large amount of work[17] has been done in correcting the Winkler method for nitrites and organic matter, no attention appears to have been given to the possibility of interference from other sources. Iron salts, for example, would be expected to interfere with an iodometric titration. Whether this interference is quantitative, and hence possible of correction by calculation, is not apparent from the literature.

The authors had met with the interference of iron salts in attempting to determine the dissolved oxygen in a stream polluted with waste liquor from a galvanizing plant as well as domestic sewage. Since no solution of the difficulty was found in the literature the question was submitted to the following investigation:

EXPERIMENTAL

A series of glass-stoppered bottles containing distilled water, potassium iodide, acid, and iron salts was set up. The amounts of iron in the respective bottles varied from 0 to 170 p. p. m., as shown in the table. They were allowed to stand and then titrated with standard thiosulfate solution. The results are shown in Table I.

TABLE I

In all cases 4 cc. concentrated HCl, 450 cc. distilled water, and 10 cc. KI solution (1 cc. = 0.03994 gram KI) were used, together with indicated amount of iron solution (1 cc. = 0.0100294 gram iron); shaken, allowed to stand 12 hours, and titrated with $Na_2S_2O_3$ solution (0.01317 *N*)

No.	Iron Solution Cc.	$Na_2S_2O_3$ Solution for 100 Cc. Water (Av. of 2 Titrations) Cc.	$Na_2S_2O_3$ for Bottle Cc.	Iron in Original Solution P. p. M.	Iron Reduced P. p. M.	Iron Reduced Per cent	Apparent Dissolved Oxygen P. p. M.
1	0	0	0.0	0.0	0.0	0.0	0.0
2	1	2.74	12.74	21.5	20.2	93.5	2.89
3	2	5.47	25.49	43.0	40.3	93.7	5.77
4	4	10.04	46.99	85.7	74.1	86.5	10.58
5	5	12.52	58.72	106.9	92.4	86.4	13.20
6	7	16.37	77.10	149.3	120.8	80.8	17.25
7	8	17.88	84.39	170.0	131.9	77.6	18.85

Since many unpolluted waters contain appreciable amounts of iron but seldom as much as 20 p. p. m., the smallest amount used in the first series, another series was run with smaller amounts varying the iron from 0 to 20 p. p. m., in order that the entire range of probable conditions might be covered. These results are shown in Table II.

That iron affects the determination of dissolved oxygen by the Winkler method is apparent from the foregoing data. This effect may be brought about in two ways. First, when present in large amounts it requires so much of even strong potassium permanganate to oxidize it from the ferrous to ferric condition that the dissolved oxygen in the reagent itself is appreciable; second, when oxidized to the ferric state it serves as an oxidizing agent itself and will oxidize the iodide ion to free iodine which will give high results.

The chief objection to the use of the Winkler method when iron is present is due to the second effect. If all the iron present were reduced and the amount of iron present were known, it would be possible to correct the titration with thiosulfate. If, however, the reaction

$$Fe^{+++} + I \rightleftharpoons Fe^{++} + {}^1/_2 I_2$$

does not go to completion, then the correction will not equal the amount of iron present. From the tables it will be seen that as the amount of iron increases a smaller percentage of the iron is reduced (seventh column). This means then that if we were to apply a correction in the Winkler method when iron is present, we should know not only the iron content, but also the percentage which acts on the iodide solution forming free iodine. Such a percentage value would vary with the temperature and foreign substances present, as well as with iron, hydrogen-ion, and iodide-ion concentration in solution. Table II shows that at a concentration of 2 p. p. m. all the iron in solution is reduced and the reading on titration with thiosulfate will be increased directly as the amount of iron present.

TABLE II

In all cases 4 cc. concentrated HCl, 450 cc. distilled water, and 10 cc. KI solution (1 cc. = 0.03994 gram KI) were used, together with indicated amount of iron solution (1 cc = 0.001003 gram iron); shaken, allowed to stand 12 hours, and titrated with $Na_2S_2O_3$ solution (0.01308 *N*)

No.	Iron Solution Cc.	$Na_2S_2O_3$ Solution for 100 Cc. Water (Av. of 2 Titrations) Cc.	$Na_2S_2O_3$ for Bottle Cc.	Iron in Original Solution P. p. M.	Iron Reduced P. p. M.	Iron Reduced Per cent	Apparent Dissolved Oxygen P. p. M.
1	0	0.00	0.00	0.00	0.00	0.0	0.00
2	1	0.30	1.40	2.16	2.20	100[a]	0.31
3	2.5	0.70	3.27	5.38	5.13	95.4	0.73
4	5	1.36	6.38	10.69	9.96	93.2	1.42
5	7.5	1.99	9.38	15.95	14.57	91.3	2.08
6	10	2.55	12.09	21.16	18.68	88.3	2.67
Tap water		0.49	...	About 2	...	..	0.51

[a] Excess 0.04 p. p. m. reduced iron over actual iron in solution is within titration error

Ferric iron on being reduced to the ferrous condition releases one equivalent of iodine per atom of iron.

$$Fe^{+++} + HI = Fe^{++} + {}^1/_2 I_2$$

Oxygen, on reacting with manganese hydroxide forming the higher hydroxide which subsequently reacts with the iodide solution, releases one equivalent of iodine per one-half atom of oxygen.

$$^1/_2\,Mn(OH)_2 + {}^1/_2\,O + {}^1/_2\,H_2O = {}^1/_2\,Mn(OH)_4$$
$$^1/_2\,Mn(OH)_4 + HI + {}^1/_2\,H_2SO_4 = {}^1/_2\,MnSO_4 + I + 2H_2O$$

Therefore, one atom of iron equals one-half atom of oxygen, or 56 grams Fe = 8 grams O.

$$8/56 \times \text{grams Fe} = \text{grams } O_2$$

The presence of one part per million of iron would indicate 0.14 p. p. m. dissolved oxygen more than is actually present. Since only about 90 per cent of the iron is converted the correction would be a little lower. Although in most cases this correction is smaller than the error in titration in the field, when the amount of iron is high as in the discharge from iron and steel works, it amounts to an appreciable error.

There is another way in which iron affects the Winkler method. The thiosulfate may react with the ferric iron itself directly according to the equation:

$$2Na_2S_2O_3 + 2FeCl_3 = 2NaCl + 2FeCl_2 + Na_2S_4O_6$$

However, most of the ferric iron has been reduced before this titration is made, so the error due to this cause is rather small, especially in low iron-bearing waters. From the equation it is seen that the error in the titration will be the same as if that amount of iodine is actually present, since the reaction is almost complete to the right.

Since the Winkler method apparently could not be modified for use in the presence of iron, the next step was to investigate some other method.

Of those mentioned above the Levy-Mohr[8] method seemed to be the one most likely to work in the presence of iron, since an iron solution is added during the procedure and therefore any iron already in the water should have no effect.

As to the accuracy of the Levy method and its modifications there is considerable difference of opinion. The Metropolitan Sewage Commission of New York[18] has used it and found close agreement with gasometric methods. Letts and Blake[9] claim high results in the presence of nitrites or organic matter, while others, such as Chlopin,[19] and Tiemann and Preusse,[20] maintain that it gives low results, the magnitude of the error depending on the amount of time allowed for the precipitate to stand, the degree of pollution of the water and the temperature at which the experiment is run. The longer the precipitate is allowed to stand before acidification the less the error. Waters run at higher temperature have given higher results than some run at a lower temperature, which is contrary to the law of solubility of gases.

With the end in view of seeing how variable amounts of iron affected the Levy method, a series of runs was made varying the amount of iron both in distilled and polluted water. The samples were tested by the Levy method, Letts and Blake modification, and also by gasometric methods.[21] The results are shown in Table III.

TABLE III—COMPARISON OF LEVY AND BOILING OUT METHODS

No.	Iron P.p.M.	Levy P.p.M.	Boiling P.p.M.	Levy[a] Cc.	Boiling[a] Cc.	REMARKS
			Distilled Water			
1	107	7.70	7.68	5.39	5.38	
2	81	7.35	7.65	5.15	5.35	
3	54	7.56	7.36	5.29	5.15	
			Raw Sewage			
4	81	0.77	0.86	0.54	0.60	Shaken with iron solution and allowed to stand for a few hours
5	54	0.35	0.43	0.25	0.30	
6	27	0.28	0.22	0.20	0.15	

[a] At normal temperature and pressure.

There is in general a close agreement in the results by the two methods. Whether or not the criticisms of this method are false cannot be judged without a much fuller investigation. The data, however, show that the Levy method can be used in the presence of iron and will give far more accuracy than the Winkler method, Rideal and Stewart modification. For instance, a water containing 107 p. p. m. (Table III) which gives a correct value for the dissolved oxygen by the Levy method would give (Table I) a value about 10.6 p. p. m. too high by the Winkler method if allowed to stand some time before titration with thiosulfate.

Another phase of the problem to be studied in this laboratory is the effect of time on the equilibrium of iron and hydrogen iodide. It is thought that it plays a considerable part.

CONCLUSION

Determination of dissolved oxygen with the Winkler method, Rideal and Stewart modification, gives high results in the presence of iron.

A correction cannot be made for iron by lowering the results in proportion to the iron present. The equilibrium

$$Fe^{+++} + HI \rightleftharpoons Fe^{++} + \frac{1}{2}I_2$$

must be considered.

Reaction gives 75 to 90 per cent of iron as iodine. Thus, the presence of 1 p. p. m. iron causes a high value of 0.10 to 0.13 p. p. m. in the oxygen.

The Levy method gives accurate results in the presence of iron and organic matter, while the Winkler method gives too high results.

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Fractional Distillation Apparatus[1]

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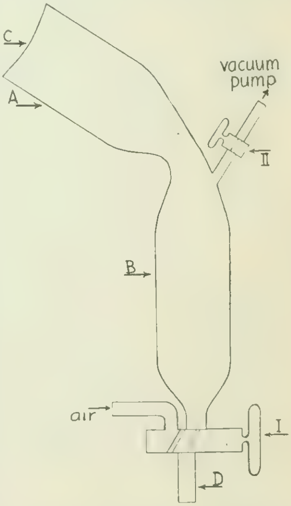
THE types of apparatus used for fractional distillation under diminished pressure, such as bird cages and other varieties designed by Kolbe, Wechmar, Gautier, and others,[2] are expensive, very inconvenient when large quantities of distillate are to be obtained, and often fragile. The following apparatus, which is merely a modification of that used by Fischer and Harries,[3] has several advantages. It is very inexpensive, easy to manipulate, is not fragile, and with it distillates of any size may be obtained.



As shown by the diagram, the apparatus may be made with an adapter, *A*, a pipet, *B*, and two stopcocks, I and II. The adapter is connected with the condenser at *C* and the receiver, which may be of any size depending upon the quantity of distillate, is attached at *D*. The apparatus is connected to a vacuum pump at stopcock II. After the first fraction is obtained, stopcock I is turned to admit air into the receiver. During the exchange of receivers, the distillation may be continued, the distillate collecting in the pipet. Distillation will only momentarily stop while the second receiver is being evacuated. When heavy liquids are to be distilled, it is well to have the bore of stopcock I, which leads to the receiver, of good size.

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[1] Received May 17, 1923.

[2] Houben-Weyl, "Die Methoden der organischen Chemie," Vol. **1**, 2nd ed., p. 567.

[3] *Ber.*, **35**, 2158 (1902).

Correlation of High School and College Chemistry

Preliminary Report of the Committee on Chemical Education of the American Chemical Society

The Committee on Chemical Education of the American Chemical Society which has been charged, during the past year, with correlating courses of high school and college chemistry, had its first official session at New Haven at the spring meeting of the Society. The committee decided that the four following objectives would help most in solving the correlation problem:

1—To encourage the teaching of chemistry in the high school.
2—To have such a course given in high school that it would answer for students who go to college as well as for students who do not go to college.
3—To outline a minimum high school chemistry course, taking into account both content and method.
4—To have colleges recognize high school chemistry, at least to the degree of having a different course for those students who have had the said outlined high school course.

These four points were taken before the Section of Chemical Education and after some discussion were approved, and hence the committee began to make plans for their development. The most direct point of contact was the preparation of the high school outline which the committee has termed "A Standard Minimum High School Course in Chemistry."

The following objectives have governed the committee in its work:

1—To prepare an outline for high school chemistry which is satisfactory for students who wish to get a general knowledge of chemistry as well as for those who are going to college.
2—To list only the minimum essential topics which are common to all localities, so that the high school teacher will have time in developing the course to supplement these minimum topics with material which he considers especially suitable for his locality or for the future work of his students. See list of topics for supplementary work at end of this report.
3—To prepare an outline which would cover the essentials of any State requirements.
4—To prepare an outline which would be in tune with the syllabus of the College Entrance Examination Board.

It is the anticipation of the committee that the following objectives will govern the high school teacher in developing the outline:

1—To show the service of chemistry to the home, to health, to medicine, to agriculture, to industry, etc.—in a word, to show the service of chemistry to the Nation.
2—To develop this service in chemistry around these minimum standard topics, and, in doing so, to see that these minimum requirements are so well taught that they may be built upon as a foundation in college.
3—To use his own order of developing the listed topics.
4—To train the student in keen observation and exact reasoning.
5—To develop a careful correlation between recitation and experiment with the minimum amount of repetition.
6—To encourage students to keep notebooks which shall be an accurate record of laboratory experiences expressed in concise, clear English.
7—To encourage chemistry being placed in fourth year of high school after the students have had a year of general science, and a year of biological science or physics, or preferably both.
8—To build upon the earlier science courses and knit them together in the best possible manner.
9—To encourage students to use reference books in addition to their textbook.
10—To help pupils to find themselves—i. e., to discover whether they have an aptitude for further study in chemistry or applied science, and, if so, to encourage such students to continue their study of science in university or technical school.
11—The teacher is urged throughout the course to stress the general principles involved in the specific cases studied.

Topics for a Standard Minimum High School Course in Chemistry

1 Water
  (a) General distribution
  (b) Physical properties: color, odor, taste, density, boiling point, freezing point
  (c) Solution: solvent, solute, saturated solution, process of solution, degrees of solubility, factors affecting the solubility of a substance, suspensions
  (d) Impurities in water: what constitutes impurities; purification by boiling, distillation or filtration
  (e) Crystallization: water vapor, water of hydration, deliquescence and efflorescence
  (f) Chemical properties: quantitative composition of water by electrolysis and by synthesis from copper oxide, contrast of physical and chemical change, contrast of elements and compounds; stability of water; interaction of water with active metals; order of activity; interaction with oxides

2—Oxygen
  (a) Preparation
    Electrolysis of water
    Industrial
    Potassium chlorate (use of catalytic agent)
  (b) Properties
    Physical: color, odor, solubility in water, weight relative to air, weight of 22.4 liters
    Chemical: tendency to form oxides in air and in oxygen, explanation of oxidation and combustion, kindling temperature
  (c) Uses: necessary to life
  (d) Ozone, briefly as to its preparation, properties, and uses

3—Hydrogen
  (a) Preparation
    Electrolysis of water
    Industrial
    Action of certain metals—i. e., sodium—on water
    Replacement in acids by metals
  (b) Properties
    Physical: as with oxygen
    Chemical: burns in air, reduction by hydrogen
  (c) Uses (practical): oxyhydrogen flame, balloons, hydrogenation of oils
  (d) Hydrogen peroxide, briefly as to its preparation, properties, and uses

4—Laws, Hypotheses, and Theories
  (a) Law of Conservation of Mass
  (b) Law of Definite Composition (proportion)
  (c) Atomic Theory (simple treatment), including electron
  (d) Law of Boyle and Law of Charles, treated briefly with special reference to gases, not experimentally, but rather their application to the interpretation of change of volume
  (e) Law of Gay-Lussac and Avogadro's Hypothesis

5—Symbols, Weight, and Volume Relations
  (a) Atomic weights (not their experimental derivative), use in performing simple chemical calculations
  (b) Molecular weights as explained by Law of Gay-Lussac and Avogadro's hypothesis
  (c) Symbols and formulas (not their experimental derivative), especially their use in writing equations
  (d) Valence, with special reference to writing formulas
  (e) Equations and their use in expressing chemical changes, including gravimetric and volumetric equations
  (f) Problems involving (1) percentage composition, (2) weights of substance and volume of gases concerned in chemical reactions, and (3) the laws of gases
  (g) Five kinds of chemical changes: direct combination, decomposition, simple replacement, double replacement, and oxidation and reduction
  (h) Formulas and writing of equations for reactions already studied

6 Air
  (a) Percentage of oxygen and nitrogen by weight and by volume
  (b) Test for water vapor and carbon dioxide
  (c) Liquid air
  (d) Evidences that air is a mixture and not a compound

7—Nitrogen
  (a) Occurrence
  (b) Properties
    Physical
    Chemical: nonsupporter of combustion, general inactivity, tests

- (*c*) Nitrogen fixation, as illustrated by plants, synthesis of ammonia, and oxides of nitrogen
- (*d*) Uses (practical)

8—Oxides of Nitrogen

- (*a*) Nitric oxide: preparation, properties, tests, and uses
- (*b*) Nitrogen peroxide: preparation, properties, tests, and uses

9—Nitric Acid

- (*a*) Preparation
  - Industrial (from the air)
  - Sodium nitrate with sulfuric acid
- (*b*) Properties
  - Chemical: action of dilute and concentrated nitric acid on copper and silver, test for nitric acid or a nitrate, decomposition products of different nitrates
- (*c*) Uses: aqua regia, oxidizing agent, nitrocellulose industries, high explosives (briefly)

10—Ammonia

- (*a*) Preparation
  - Decay of nitrogenous matter
  - Industrial (Haber process)
  - Destructive distillation of soft coal
  - Action of ammonium salt with nonvolatile base
- (*b*) Properties
  - Physical
  - Chemical: basic character of water solution, ammonium radical formation of ammonium salts, test
- (*c*) Uses: refrigerating agent, preparation of ammonia water

11—Acids, Bases, and Salts

- (*a*) Properties
  - General: taste, action on litmus, etc.
- (*b*) Normal and molar solutions
- (*c*) Activity of acids and bases
- (*d*) Solutions, conductors of electric current

12—Theory of Ionization (briefly)

- (*a*) How theory explains electrolysis
- (*b*) How theory explains neutralization
- (*c*) Acid and base defined in terms of ions
- (*d*) Atom and ion distinguished
- (*e*) Chemical equilibrium
- (*f*) Reversible reactions
- (*g*) Why reactions go to completion
- (*h*) Common ion effect

13—Sulfur

- (*a*) Occurrence
- (*b*) Extraction: American method (Frasch method)
- (*c*) Allotropic forms: rhombic, prismatic, and amorphous, flowers of sulfur
- (*d*) Properties
  - Chemical: direct combination with copper, iron, and zinc
- (*e*) Comparison with oxygen
- (*f*) Uses: vulcanizing rubber, making matches, making sulfur dioxide

14—Oxides of Sulfur

- (*a*) Sulfur dioxide
  - Preparation: burning sulfur, roasting of sulfide ores, action of an acid upon a sulfite
  - Properties
    - Physical
    - Chemical: action with water (sulfurous anhydride test)
  - Uses: bleaching, reducing agent
- (*b*) Sulfur trioxide
  - Preparation (industrial)
  - Catalysis as illustrated by its manufacture
  - Properties, including test
  - Uses

15—Sulfuric Acid

- (*a*) Preparation
  - Lead chamber process with simple chamber reactions only
  - Contact process
- (*b*) Properties
  - Physical: specific gravity and boiling point
  - Chemical: affinity for water, dilute acids on metals and concentrated acids on copper, test for SO_4 ion
- (*c*) Uses: preparation of other acids, with reason for the same; manufacture of fertilizers; refining of petroleum

16—Hydrogen Sulfide

- (*a*) Preparation: ferrous sulfide and dilute hydrochloric or sulfuric acid
- (*b*) Properties
  - Physical
  - Chemical: combustion, action on metals, action on salt solutions of metallic salts
- (*c*) Uses: precipitation of sulfides with special reference to testing for certain metals

17—Periodic Table for Classification Only

- (*a*) Elements arranged in order of atomic weights
- (*b*) Relation of valence to group numbers
- (*c*) Gradual transition from metals to nonmetals in passing from Group I to Group II
- (*d*) Increase of metallic nature with increase of atomic weight within the group

18—Halogens

- A. Chlorine
  - (*a*) Preparation: one industrial method, one laboratory method—oxidation of hydrochloric acid using a chloride and manganese dioxide
  - (*b*) Properties
    - Physical
    - Chemical: direct combination with other elements to form chlorides, tests, comparison with oxygen
  - (*c*) Uses: bleaching and disinfecting action
  - (*d*) Compound: hydrochloric acid (gas and solution)
    - Preparation: a chloride and sulfuric acid
    - Properties
      - Physical
      - Chemical: a typical acid shown by taste, action on litmus, and reaction with metals; test for chloride ion
    - Use
- B. Bromine and iodine
  - (*a*) Preparation contrasted with chlorine
  - (*b*) Comparison of physical and chemical properties of chlorine, bromine and iodine; relative replacement; tests
  - (*c*) Uses of iodine
  - (*d*) Position of halogens in the periodic table

19—Carbon

- (*a*) Occurrence
  - General distribution
  - Allotropic forms: diamond, graphite, amorphous forms
- (*b*) Commercial preparation of useful forms: graphite, charcoal, lampblack, coke, diamond, bone black
- (*c*) Properties
  - Physical
  - Chemical: affinity for oxygen, action with calcium and silicon
- (*d*) Uses: common fuels including carbon or carbon compounds, operation of household stoves and furnaces, reduction by carbon, decolorizer, adsorbent

20—Carbon Dioxide

- (*a*) Occurrence: relation to plant and animal life
- (*b*) Preparation: burning carbon or a carbon compound, action of acid on a carbonate
- (*c*) Properties
  - Physical
  - Chemical: nonsupporter of combustion, action with soluble hydroxide, brief treatment of its solubility in water, its role in nature, plant growth, temporary hard water, and test for carbonate ion
- (*d*) Uses: refrigerating, beverages, fire extinguishers, leavening agent in bread-making

21—Carbon Monoxide

- (*a*) Preparation: from oxalic acid, reduction of carbon dioxide by carbon
- (*b*) Properties
  - Physical
  - Chemical: combustibility, reducing power, test
- (*c*) Uses: reducing agent industrially; constituent of water gas, coal gas, and producer gas
- (*d*) Illuminating and fuel gases: manufacture and uses

22—Sodium

- (*a*) Preparation
  - Industrial: electrolysis of sodium hydroxide
- (*b*) Properties
  - Physical: metallic luster, hardness, color, power to conduct heat and electricity
  - Chemical: flame test; action with water, with chlorine
- (*c*) Compounds of sodium
  - Hydroxide: commercial preparation (either lime soda or electrolytic process); properties as typical base; neutralization; test for hydroxyl ion; use (cleaning agent, soap-making)
  - Chloride: occurrence in sea water and mines; laboratory preparation; uses; role in industry
  - Carbonate: preparation by Le Blanc and Solvay process; properties; use (particularly industrial)
  - Acid carbonate: preparation (laboratory and industrial); properties; uses; baking powders
  - Nitrate: occurrence; properties; uses

23—Calcium Compounds

- (*a*) Carbonate:
  - Occurrence: marble, limestone, shells
  - Properties: solubility in water containing carbonic acid (temporary hard water), decomposition by heat, action with acids

Industrial uses: building material, making of quicklime, flux in iron furnaces, glass

(*b*) Oxide: preparation (industrial); properties; industrial uses

(*c*) Hydroxide: preparation; properties; uses (mortar, its hardening)

(*d*) Sulfate: occurrence; properties; test; uses; permanently hard water and contrast with temporary

(*e*) Bleaching powder: commercial preparation; uses, (bleaching, disinfecting)

(*f*) Calcium phosphates: preparation; uses (fertilizers)

(*g*) Fertilizers: presence of potassium, nitrogen, and phosphorus as ingredients

24—Iron

(*a*) Metallurgy (extraction from oxide ores—pig iron—blast furnace)

(*b*) Cast iron: physical properties

(*c*) Uses of cast iron: castings, etc.

(*d*) Steel: manufacture (Bessemer, open hearth, and electrical processes); varieties of iron and steel with reference to their industrial uses

(*e*) Protective coatings to prevent corrosion of iron and steel: tin (tin ware), zinc (galvanized iron), nickel plate, enameled ware, paint

(*f*) Compounds of iron
  Oxides: occurrence and uses
  Hydroxide: preparation (laboratory); properties; uses
  Sulfate: preparation; properties, uses
  Chlorides (ferrous and ferric): preparation (laboratory); properties; uses; ferrous and ferric compounds; oxidation and reduction of iron compounds; change of valence

25—Zinc

(*a*) Metallurgy from carbonate and sulfide

(*b*) Properties
  Physical
  Chemical: action with dilute acids, electromotive series

(*c*) Uses: alloys, primary cells

26—Aluminium

(*a*) Metallurgy (electrolytic process)

(*b*) Properties
  Physical
  Chemical: action with hydrochloric acid and sodium hydroxide, amphoteric

(*c*) Uses: utensils, alloys

(*d*) Compounds
  Hydroxide: preparation (laboratory); properties; uses; purification of water
  Sulfate (alum): preparation (laboratory); properties; uses

27—Copper

(*a*) Preparation (outline of process only with reference to iron)

(*b*) Purification by electrolysis

(*c*) Electroplating

(*d*) Properties
  Physical
  Chemical: action with air and acids

(*e*) Uses: electrical purposes, alloys

(*f*) Compounds of copper
  Sulfate: properties; uses (water purification, fungicide)

28—Compounds of Lead

(*a*) Properties

(*b*) Uses

(*c*) Compounds
  Lead monoxide: preparation; properties; uses
  Basic lead carbonate: industrial preparation; properties; uses (paint)

29—Sources of Organic Compounds

(*a*) Destructive distillation of wood: methanol, acetic acid, charcoal

(*b*) Destructive distillation of coal: gas, ammonia, benzene, tar, coke

(*c*) Distillation and cracking of petroleum: gasoline, kerosene, vaseline, paraffin

30—Organic Compounds

(*a*) Sugar; (*b*) Starch; (*c*) Acetic acid (briefly)

OPTIONAL LIST

Shall these topics be included? If so, to what extent? Opinions are solicited.

Arsenic
Colloids
Electrolysis
Electronic structure of matter
Energy change
Fehling's solution
Mercury
Other alloys than those contained in copper
Periodic law
Phosphorus
Rare gases of air
Reacting weights (not atomic)
Silver
Zinc chloride
Zinc oxide
Zinc sulfate

LIST OF TOPICS FOR SUPPLEMENTARY WORK

Glass. Crown, flint, lead, special glasses, coloring of glass

Clay Products. Brick, pottery, chinaware, porcelain

Artificial Stone. Lime, plaster, mortar, hydraulic cement, concrete stucco, plaster of Paris

Fertilizers. Problems of soil fertility, elements needed by growing plant and function of each. Photosynthesis and carbon dioxide cycle. Nitrogen cycle and function of nitrogen fertilizers. Use of limestone and phosphate rock

Coal. Composition and fuel values of different varieties. Distillation of coal tar, light oil, middle oil, heavy oil, tar, pitch. Relation to dyes and explosives

Petroleum. Fractional distillation into burning oils, solvent oils, lubricants, paraffins. Problem of gasoline supply and possible exhaustion of petroleum

Wood. Distillation of wood to produce methanol, acetone, acetic acid, charcoal

Explosives. Black powder, nitroglycerol, dynamite, guncotton, trinitrotoluene. Relation to nitrogen fixation by arc, Haber, and cyanide processes

Paint, Varnish, Etc. Oil paints and driers, varnish, shellac, copal, linseed oil, oil cloth, linoleum

Pigments. White lead, red lead, iron oxide, lead chromate, etc.

Textile Fibers. Natural and artificial silk. Wool: scouring, bleaching, felting, etc. Cotton: bleaching, mercerizing, etc.

Dyeing. Direct and mordant dyes

Cleansing Agents. By acid: oxalic, hydrochloric. By alkalies: caustic soda, soap emulsification. By special solvents: carbon tetrachloride, benzene. Composition of trade-marked cleaning fluids

Photography. Blueprints, plates, films, prints, toning, etc.

Food Constituents. Starch preparations from corn; cooking to dextrin and to paste, hydrolysis to glucose

Sugars. Preparation and refining of beet and cane varieties; conversion to caramel; inversion

Fats. Olive oil, cottonseed oil, butter, oleomargarine, hardening oils by hydrogenation

Proteins. Albumins, casein, gluten, peptones, gelatin, vitamins

Beverages. Charged waters, soda, mineral, infusions, tea, coffee, fruit juices (artificial flavors), fermentation

Poisons and Common Antidotes. Common inorganic drugs

Leavening Agents. Yeast, soda, baking powders

Matches. Ordinary and safety types

Adhesives. Gums, paste, dextrin, glue, casein, water glass (sodium silicate)

Inks. Various types

Refuse Disposal. Sewerage garbage; fermentation and putrefaction; civic problems; disinfectants and deodorizing agents

Preserving. Sterilizing, pasteurizing, desiccating, pickling by salt and sugar; chemical preservatives and tests for them

Metals. Extraction processes; oxide ore, iron, sulfide ore, lead; electrolysis, sodium and aluminium; extraction of other metals may be studied by comparison with these

Metals. Used for basic purposes, iron, copper, aluminium, lead; for ornament, gold, silver, nickel; for alloys, bronze, brass, solder, type metal, antifriction or bearing metals, fusible metal

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The purpose of placing this preliminary report in THIS JOURNAL is to give every chemist an opportunity to criticize it. There will be subcommittees in various sections of the country where arrangements will be made for tabulating such criticisms. If such opportunity is not offered, suggestions may be sent directly to the chairman of the national committee, Neil E. Gordon, University of Maryland, College Park, Md.

NEIL E. GORDON, *Chairman*
B. S. HOPKINS
J. R. KUEBLER
L. W. MATTERN
L. C. NEWELL
W. D. RICHARDSON
R. E. ROSE
WALTER SCHMIDT
W. SEGERBLOM
R. E. SWAIN

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[1] "Reorganization of Science in Secondary Schools," Bureau of Education, *Bull.* 26 (1920).

At its recent annual meeting, the American Pharmaceutical Association made the following grants for the year 1923–24:

To E. Kremers and K. H. Rang, of the University of Wisconsin, for work on decolorized tincture of iodine and on such other preparations of the National Formulary as time permits—$250.00.

To W. J. McGill, of the University of Michigan, for work on the electrometric titration of alkaloids—$200.00.

These research grants are made annually from the interest accruing from the association's research fund, which represents the profits accruing from the sale of the National Formulary.

The New Patent Act in Canada[1]

By Clayton L. Jenks

120 Broadway, New York, N. Y.

THE Canadian patent law which went into force on September 1, 1923, is so different from the old law that an American inventor or manufacturer may now find it worth while to adopt an entirely new attitude towards the Canadian market.

Heretofore, Canada discriminated against foreigners rather severely. Under the old law, a Canadian patent became void if an article covered by the patent was imported into Canada one year after the patent was granted. Furthermore, the holder of a patent was required to manufacture in Canada within two years of the patent date, unless the patentee voluntarily agreed to grant licenses to Canadian manufacturers.

Under the new law, a patent is not automatically invalidated by reason of importation, and the working requirements, which are patterned after the British, are more liberal.

Working Requirements

A patent is now granted under certain conditions which may be summarized as follows, ignoring many of the finer points:

(*a*) The patentee shall manufacture the invention, or work the process, in Canada sufficiently to satisfy the reasonable requirements of the public.

This implies that one need not work the patent until there is a public demand for the invention. Hence an inventor of a new product is no longer under any compulsion to manufacture in Canada within a specific time limit whether or not his manufacturing and marketing plans have been developed.

(*b*) Any interested person may petition the Patent Commissioner, stating that the reasonable requirements of the public have not been satisfied, and ask that the patentee be ordered to supply the patented article at a reasonable price or to grant licenses for using the invention on reasonable terms.

(*c*) If the parties do not come to an agreement, the Commissioner may, after giving a hearing, order the patentee to supply the article within reasonable limits at a price fixed by the Commissioner or to grant a license. This must be done within a specified time limit on pain of forfeiture of the patent.

(*d*) Such an order shall not be made within three years of the patent date, or before June 13, 1924; nor will it be made if the patentee gives satisfactory reasons for his default.

(*e*) The reasonable requirements of the public shall not be deemed to have been satisfied:

If any trade or industry in Canada is unfairly prejudiced by the patentee's failure to supply the article or carry on the process; or

If the patentee will not grant a license on reasonable terms; or

If he attaches unfair conditions to the purchase or use of the invention.

(*f*) Not less than three years from the date of the patent grant, and after June 13, 1924, any one may petition the Commissioner to have the patent revoked on the ground that the invention is being worked mainly outside of Canada.

(*g*) In such a case, if the patentee cannot furnish a satisfactory excuse for not manufacturing in Canada, the patent may be revoked at once, or after a reasonable interval, unless the patentee has begun working operations in Canada by that time.

These provisions of the patent law are new and have not been clearly interpreted as yet, but it is to be noted that the Commissioner has been given wide latitude and discretion in the matter. Since patentees living in this country have not been unduly oppressed in the past, and since the new law is less drastic than the old, it is fair to assume that the Commissioner will apply the law reasonably and without imposing a heavy burden on United States inventors and manufacturers.

Patent Applications

Since Canadian patent practice differs considerably from that on this side of the line, a resumé of some of its main features as now required seems worth while. Ordinarily, an American files his patent application first in this country; hence the law affecting such cases should be particularly noted. The main requirements are that:

(*a*) The patent application in Canada must be filed within one year after the filing date of the United States application.

(*b*) The invention must not have been patented or described in any printed publication more than two years before the date of filing in Canada.

(*c*) The invention must not have been in public use or on sale in Canada for more than two years before the filing date.

It should be noted that public use or sale in any country other than Canada does not affect one's right to a patent, whereas a published disclosure of the invention in any country counts against him. The inventor may use or sell his invention in the United States for more than two years before filing in Canada, but he must be careful that no description of the invention has been published anywhere in the world for that length of time, if he wishes to obtain a valid patent.

In order that the new law may not work undue hardships on applicants, it gives until June 13, 1924, within which time inventors who have already filed United States applications may file their Canadian cases, providing the requirements concerning two years' public use, sale, and printed disclosure are satisfied. The law in regard to filing such applications where a United States application has been filed for more than a year may be summarized as follows:

(*a*) If no United States patent has been granted, the Canadian application must be filed before June 13, 1924.

(*b*) If a United States patent has been granted the Canadian application must be filed within one year from the date of the patent and before June 13, 1924.

The Examiner does not search any but Canadian patents; hence it is always advisable to file the United States application first and get the benefit of the search made at Washington before the Canadian case is filed. In fact, it is wise to hold up the latter after filing until the patentability of the claims in this country can be determined, so that the Canadian claims may be made to correspond with those in the United States case.

Since the Canadian Office does not print its patents, the applicant is required to file duplicate copies of the specification and drawings, as well as a third copy of the drawings and of the patent claims. One of the duplicate copies of the complete application is held in the Patent Office when the patent is granted, and the other copy is attached to the patent-granting paper and returned to the inventor. When one wishes to obtain copy of such patent, it is necessary for the Patent Office to make a typewritten or photographic copy of the specification and a photograph of the drawings for such purpose. This costs $4.00 as against ten cents for a United States patent.

Foods and Medicines

Of direct interest to chemists, it may be noted that if the invention relates to a food or medicine prepared by a chemical process, the inventor should claim the method of manufacture and he may not claim the substance itself, except when produced by the special method described and claimed.

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[1] Received October 6, 1923.

Each patent for the preparation of a food or medicine shall be subject to a compulsory license granted by the Commissioner. Any person applying for this license may be permitted to use the invention for the production of food or medicine, but not otherwise. So wide are the powers of the Commissioner that he may settle the terms of the license, the law merely stipulating that he have due regard to the desirability of placing the substance in the hands of the public and at the same time giving the inventor a proper reward for his invention.

INTERFERENCES

If two independent inventors file applications covering the same invention, a board of arbitrators shall be appointed to award the patent to one of the claimants. In the United States, such a decision is rendered by a special official in the Patent Office, from whose decision one may appeal to various other officials and the courts. In Canada, one of the arbitrators is chosen by each applicant and the third by the Commissioner. If either applicant fails to choose his arbitrator, the patent shall issue to the other. If there are more than two claimants, the Commissioner may appoint the three arbitrators, provided the claimants do not unite in selecting them. The arbitrators are given the full powers vested in a Civil Court to investigate the matter and the award signed by any two of the three arbitrators shall be final.

RESTORATION AND REISSUE OF PATENTS

If a Canadian patent has become void under the terms of the old patent act, through failure to pay fees or to manufacture in Canada or because of importation, the patentee has a chance under the new act to have his patent revived within two years from the date of its becoming void, but any third party who has commenced lawfully to make, use, or sell in Canada, during the period when the patent was void, may continue to use the invention just the same as if the patent had not been revived.

A reissue to correct inadvertent mistakes in a patent must be obtained within four years from the date of the patent; but any patent which is now alive may be reissued if the application is filed before June 13, 1924. This provision is important, since it gives a patentee whose Canadian patent was granted before his United States patent an opportunity to revise the Canadian patent in agreement with the other case and thus incorporate in it such claims as have stood the test of patent searches in this country.

VALUE OF A CANADIAN PATENT

Canada is a country of about 9,000,000 people and has over 40,000 miles of railroads. In many industries its importance for manufacturing purposes is far out of proportion to its population, since the United Kingdom is its market. The decision, therefore, whether or not to take out a Canadian patent should be made only after considerable study into the advantages of manufacturing in Canada, or of licensing a Canadian under the patent, as well as the particular conditions which affect the market in Canada and the British Empire.

Since the patent cannot be attacked for at least three years, that period may be sufficient for one to get his market established. If an application is filed the patentee thereby secures a period of grace within which he may decide as to the value of Canadian patent protection. He can then take his time in analyzing the problem as to whether he will manufacture in Canada, grant licenses or merely do nothing and wait until the patent is attacked before taking any steps to work the patent. The last course is one that is often adopted with reference to British patents. Undoubtedly, a Canadian patent is worth while in a large number of cases.

Personals

Alan R. Albright has resigned his position in the Jackson Laboratory of the E. I. du Pont de Nemours & Company to organize a research laboratory for Gumpert & Co., Brooklyn, N. Y.

Raymond F. Bacon, C. H. Kidwell, and **Elizabeth N. Kidwell** have reorganized the firm of Kidwell & Bascom, Inc., under the name of Kidwell & Co., Inc., chemists and chemical engineers. The newly elected officers of the company are: C. H. Kidwell, president and treasurer; Raymond F. Bacon, vice president; Elizabeth N. Kidwell, secretary. The company will continue its research and consulting business at its office and laboratory at 27 Thames St., New York City.

Andrew Balfour, for the past ten years director-in-chief of the Wellcome Bureau of Scientific Research, London, resigned on October 31. **C. M. Wenyon,** who for the past nine years has been director of research in the tropics at the Wellcome Bureau of Scientific Research, has been designated as his successor.

Joseph S. Bates, formerly manager of the Research Division of the Marcus Hook, Pa., plant of the National Aniline & Chemical Co., is now employed by the Textile Service Co., Philadelphia, Pa.

Russell W. Brandt, formerly development chemist for the U. S. Gypsum Co., Fort Dodge, Ia., has taken charge of the chemical work of the General Fireproofing Co., Youngstown, Ohio.

Samuel Byall, formerly assistant research chemist at the sugar mill of Penick & Ford, Marrero, La., has resigned to become chief chemist of the International Sugar Feed Co., Memphis, Tenn.

P. G. Daschavsky, senior and supervising chemist of the laboratories of the Cudahy Co., Omaha, Neb., has found it necessary to take an indefinite leave of absence on account of continued ill health.

F. S. Dickson has resigned his position as assistant to the president of the Synthetic Organic Chemical Manufacturers Association, New York City, to go into private business.

Richard Fischer, formerly of the Chemistry Department of the University of Illinois, has accepted a position as research chemist at the laboratories of the Combustion Utilities Corp., Long Island City, N. Y.

H. C. Howard has been appointed assistant professor of chemistry in the Department of Chemistry, University of Missouri. For some time Dr. Howard has been research chemist on the staff of the B. F. Goodrich Company.

Karl G. Krech has recently been appointed assistant process superintendent of the new Parco refinery of the Producers & Refiners Corp., Parco, Wyo.

Max Kuniansky, formerly analyst for the American Cast Iron Pipe Co., Birmingham, Ala., has accepted a position as chemist with the Lynchburg Foundry Co., Lynchburg, Va.

The honorary degree of doctor of science was conferred by the University of Liverpool upon **G. N. Lewis,** professor of chemistry, University of California, during the recent meeting of the British Association for the Advancement of Science.

James W. Martin has recently resigned from the employ of the Union Carbide & Carbon Chemical Corporation to accept an appointment as assistant to the general superintendent of the Jones & Laughlin Steel Corp., Woodlawn, Pa.

August Merz, of Heller & Merz, has been elected chairman of the dyestuffs section of the Synthetic Organic Chemical Manufacturers Association, New York City, to fill the vacancy caused by the death of Fred E. Signer.

William B. Plummer, formerly research chemist for the Grasselli Chemical Co., is now associated in the same capacity with the Combustion Utilities Corp., Long Island City, N. Y.

L. W. Ryan, who for the past nine years has had charge of the research laboratory of the Lindsay Light Co., Chicago, is now employed as research chemist for the Titanium Pigment Co., Niagara Falls, N. Y.

Otto M. Smith has accepted the position of professor of chemistry at the Oklahoma Agricultural and Mechanical College, Stillwater, Okla. During the past year he was connected with the chemical department of the Iowa State College.

Richard Sneddon has left the employ of the Dominion Flour Mills, Ltd., Montreal, where he has been employed as chief chemist for the past two years, to go to California for his health. **John Miller,** formerly chemist for the Shelly Bakeries, Vancouver, B. C., has been designated as his successor.

AMERICAN CONTEMPORARIES

John Uri Lloyd

TO KNOW a man you must see him at his work. To do this in the case of John Uri Lloyd you amble down a quiet side street in Cincinnati and find the pharmaceutical manufacturing concern of Lloyd Brothers—three of them, one of whom seems to watch over the more impractical two, a second who is constantly at molds and never at business, and the third who is the subject of this sketch. To find him, you enter the business office where fast work is necessary if advance is to be made. Better an appointment ahead or else some twenty voices are likely to carry the information that the "Professor," as he is rightly, appreciatively, and affectionately called, is off the premises with no prospect in the visitor's life of return. And when a man's soul is in the spirit world is this not the truth? But if you can give the right sign—and an ability to discuss mass action is a better one than salesmanship—a friendly hand from a brother, a secretary, or a production manager urges you through a door. You choose between walking up four flights or taking the freight elevator. Again you feel lost until "Edee," who is at once cheerful presence, technical assistant, and guardian lion to the Professor, guides you with gentle voice through dark corridors into one of two or three cubicles, immaculately clean, spotlessly in order, and strictly at work. And here, either from his desk or from over some beakers the Doctor of Science, *honoris causa*, or the "Empiricist and Irregular," as he calls himself, welcomes you.

John Uri Lloyd

I do not remember a time when, either alone or with a group of scientific friends, there was not in his first words a note of appreciation for *their* endeavors—a proof at once of his first-hand knowledge of the other man's life and the catholicity of his thought, for politicians, practical men, and theorists who put the modern builders of the atom to shame, all seek him out. Such greeting is followed by, "May I tell you a story?" And then some pearl, fitting well into the setting of the moment, is brought forth from his seventy-odd years of oyster life which even the great must pass through. In the pause which follows he speaks again: "I have prepared an experiment which I should like to show you." In those who have had this experience several times, a warm rush of blood to the head is the emotional response which foretells that now some new decoration will be knocked off their scientific gargoyle. Do you hold the Guldberg-Waage law all sufficient; is the "dew" on plants a settled question for you; do you think that the tincture preparer of 1850 knew everything; is your view of solubility a crooked one because you know only water; is water itself just H_2O to you; is biology and undertaking confused in your mind; are you sure that you know where the alkaloids come from; do you know why plants are green, or sometimes red, or maybe black; or why flowers are white and sometimes yellow? Answer carefully if your philosophy, your faith, or your religion are built up on the demonstrable in nature and not upon the interpolated texts of our scientific cook-book makers.

As you wait for a solution to filter, your eyes wander into the background. What are those vials labeled *a* to *d?* "Just alkaloids separated from ———." And what are those labeled I to IX. "Another set from ———." But you were sure that each of these infernal plants contained but one alkaloid. Quite so, but here are the rest. And knowing that fat reputations have been built upon the discovery of just one alkaloid, you ask when the Professor will publish his results. "I am not young any more and a bit tired. Let me tell you about them and then you publish the facts." You see on the table a pot of tar-like material. And what is that? "Just the muck which you 'regulars' think it well to carry along with the bits of active material in your standard pharmaceuticals and which, after twenty years of work, I have learned to get out by my studies of differential solubility." You feel that you have heard just an overtone of bitterness in his voice, but a look at his face seems to belie your impression.

You digress from the material of the demonstration to its philosophic consequences, and philosophic consequences join quite naturally to the business of life itself. Is science a cloak to you which may be put on and off during convenient working hours? If so, John Uri Lloyd does not interest you for to him it is life itself. Do you find her a yoke gladly to be cast aside were the rewards of labor not so necessary? Again our man does not interest you for he follows her as lovers, romance; and children, the rainbow. Alkaloids are not things to be made into medicine, but voices which speak from another world. To be a practical man of chemistry is simply to ease the material life of a fellow that he may enjoy better the fruits of the spirit.

You rise to go. You find your way out as you came in, but you are not as conscious as you were of the externals. You are more conscious of the internals. You have lost something—some of your scientific prejudices, some of your party adherences, some of your reverences for mere tradition. Also you have gained something—a more mobile state of mind, a larger tolerance, an increased generosity. And you are conscious that this is because for a little while you have been away from commissions, committees and boards, from diagrams, formulas, and fudge, and from canned efficiency, officialism, and Main Street, and for the same length of time have lived in the presence of the one thing that moves our universe, an individual and a man who is as good a picture in flesh and blood of what science stands for as may be found in the day's journey.

Martin H. Fischer

New Tabular Data

The Editorial Office of International Critical Tables has just finished the preparation of a table of the viscosity of water at 1-degree intervals between 0° and 100° C. This table is based upon a very thorough and critical evaluation of all the data available on the subject. While prepared primarily for the use of Coöperating Experts of International Critical Tables, a number of extra copies are available for distribution at 5 cents (stamps) each. Copies of the 16-page pamphlet, entitled "Fundamental Constants and Conversion Factors," are also available at 25 cents (stamps) each. This pamphlet contains the latest data on the fundamental constants of nature, including definitions, dimensional equations, conversion factors, etc.

SCIENTIFIC SOCIETIES

Meeting of American Electrochemical Society

TWO features mark the forty-fourth meeting of the American Electrochemical Society, at Dayton, Ohio, September 27, 28, and 29, 1923, as probably the most important meeting which this Society has held. Round-table discussions of four of the major problems of the electrochemist, held behind virtually closed doors, at which all interested were invited to discuss freely and openly their problems and results, brought out an immense store of information and opinion with direct practical bearing which could not have been gotten in formal papers. The symposium on gaseous conduction, which occupied the entire second day of the meeting, brought together in one place practically all the present-day knowledge of this subject from both physicists and physical chemists.

The first session of the Society, held at the Hotel Miami, was devoted to the address of welcome by Charles H. Paul, president of the Engineers' Club of Dayton, and to the reading and discussion of six papers. Water-line corrosion was the subject of a paper by Kenneth M. Watson, which was discussed with much interest from the floor. M. A. Hunter and A. Jones have studied the reduction by sodium of various rare metal chlorides, particularly those of beryllium, chromium, zirconium, uranium, and vanadium, and suggested that this method offers a possible commercial process for producing these metals. George S. Tilley and Oliver C. Ralston followed with a discussion of electrometric methods of following hydrolytic reactions. Three papers from the research laboratory of the Westinghouse Electric & Manufacturing Company dealt with various phases of insulating and impregnating compounds used as insulators and the effect of age and heating on these. E. J. Casselman discussed the phenol-formaldehyde group; H. C. P. Weber, the varnish group; and D. E. Howes, various impregnating compounds.

Luncheon the first day was served to four groups at the Engineers' Club and was followed by round-table discussions. H. W. Gillett, of the Bureau of Mines, presided over the most interesting discussion of the group considering "Electric Furnace Brass Foundry Practice." This group consisted of representatives of the central power companies, and the designers, builders, and users of electric brass furnaces. Walter Fraine presided over the symposium on the "Development and Future of Electrodeposition;" T. J. Thatcher, over that on "Organic Electrochemistry;" and A. H. Hooker, over that on the "Utilization of Chlorine." These round-table discussions were so successful that they will be made a regular feature of the Society's meetings.

Those not detained by the round-table discussions were the guests of the local committee on a tour of inspection of McCook Field, the engineering station of the U. S. Army Air Service, and of the Miami Conservancy, the immense project which has been completed with the idea of preventing the recurrence of the floods which formerly caused much damage to the district around Dayton.

Thursday evening was devoted to a picnic dinner and smoker at Triangle Park. The feature of this dinner was the informal address of Chas. F. Kettering, president of the General Motors Research Corporation, on the future of research. In a most picturesque way, Mr. Kettering appealed for closer coöperation between the workers in the various fields of science. "What we need," he said, "is correlation among the so-called sciences. All of us are studying merely the relations of mass and energy." His plea was for the reduction of the expression of results to commonly understandable terms, rather than "the foreign languages" in which chemists, physicists, engineers, astronomers, and so forth, now express the same simple relations. He was quite vehement in his protest against "recognized authority," which he said did not exist, and stated that the more standardized an industry is the more fertile a field it offers for research.

Friday's sessions were devoted to a symposium of sixteen papers on the various aspects of gaseous conduction, under the chairmanship of Duncan MacRae. Its importance can hardly be overestimated, particularly when it is considered that papers from Holland, England, Canada, and Germany were included. The application of these studies to the X-ray, radio, and the electric lighting and electric arc industries was brought out. H. B. Wahlin brought the symposium to a fitting close with an experimental address on recent work in this field.

An intensely interesting program on the electrodeposition of metals occupied the session of Saturday morning. Papers from the Bureau of Standards, University of Pennsylvania, Niagara Electrochemical Company, Massachusetts Institute of Technology, Columbia University, University of Wisconsin, and the Northampton Polytechnic Institute of London, formed part of this program

The spring meeting of the Society will be held at the Bellevue-Stratford, Philadelphia, Pa., April 24, 25, and 26, 1924. The subjects to be discussed will include electric furnaces, recent progress in electrodeposition, and organic electrochemistry. Round-table discussions will be held as at the Dayton meeting.

Societies Elect Officers

At the annual meeting of the Technical Photographic and Microscopical Society, held at Grand Central Palace, New York City, September 21, 1923, the following officers were elected:

President: Emile M. Chamot
Vice Presidents: Frank V. Chambers, Henry Green, and Arthur W. Carpenter
Secretary-Treasurer: Alfred B. Hitchins
Executive Committee: Officers, and F. F. Renwick and Lloyd I. Snodgrass

. . . .

George K. Burgess, director of the Bureau of Standards, was elected president of the American Society of Steel Treating at the association's annual convention. The other officers named were: vice president, R. M. Bird; treasurer, Zay Jeffries; and director, J. F. Harper.

Calendar of Meetings

American Mining Congress—New York City, November 5 to 10, 1923.

Association of Official Agricultural Chemists—39th Annual Convention, Washington, D. C., November 19 to 21, 1923.

American Institute of Chemical Engineers—Winter Meeting, Washington, D. C., December 5 to 8, 1923.

American Electrochemical Society—Spring Meeting, Philadelphia, Pa., April 24 to 26, 1924.

American Chemical Society—67th Meeting, Washington, D. C., April 21 to 25, 1924.

NOTES AND CORRESPONDENCE

Sell Chemistry to America

Many chemists and physicists bewail the fact that their contributions to progress are neither understood nor appreciated and that their status in the mind of the general public is a lowly one.

At the third annual dinner of the Salesmen's Association of the American Chemical Industry, Charles H. Herty, president of Synthetic Organic Chemical Manufacturers Association, remarked that his hearers carried the chemical industry in their grips and urged them to sell it to America. Every salesman knows that it is easier to sell an article that has been well advertised than one that has had little or no publicity. At the same function Edgar Fahs Smith, provost emeritus of the University of Pennsylvania, the guest of the evening, urged the recognition of chemistry's claim as "the most human science," one that served each and every one in countless ways every day.

For the lack of recognition accorded chemical industry the chemist himself is largely to blame because he has failed to advertise the service he renders. When you meet a man who says he is a civil engineer, at once you visualize the one who builds roads through forests, spans rivers, and tunnels mountains. Parallel concepts arise when you meet the mechanical, electrical, or mining engineer. Those in other professions—doctors, lawyers, architects—all occupy positions of esteem in the mind of the public they serve, because every day that public sees examples of their products and knows them for what they are. But when Mr. Average Citizen meets one who styles himself chemist he pictures a pill-roller, or, ascending the scale of his imagination, one who can tell him how to detect wood alcohol in the bootleg he buys.

The chemist and physicist bewail the fact that they are not accorded the respect that is justly merited through their services to American industry, and yet make no well-directed or concerted effort to establish the status they claim in the public mind. Every one knows that Gustav Lindenthal conceived Hell Gate Bridge, Cass Gilbert the Woolworth Building, and A. J. Cassatt the Pennsylvania Tubes and Terminal, but how many know a single name of the many chemists and physicists, who, by long painstaking research, produced steel and cement of a quality that made possible those monumental achievements. The public accepts as a matter of course that its supplies of milk and water shall be pure and wholesome, that its foods shall be unadulterated and nourishing—what chemist has ever tried to advertise the service his science renders here? Metropolitan life as it exists today could not have been evolved had it not been for the services rendered by our chemists and physicists which alone have made possible the type of buildings in which we live and work, the kind of clothes we wear, and even modern systems of transportation and communication—and yet, relatively few people realize these facts. The day should not be very far distant when every industrial exposition held in this country should have an AMERICAN CHEMICAL SOCIETY booth, wherein will be shown, in a manner calculated to win popular attention, the principal contributions of chemistry and physics to the science, art or business whose interests are being served by that particular exhibition.

Although chemistry and physics are fundamental sciences and are employed in every industry, their importance is not grasped because their influence on ultimate products is obscure. This is particularly true if the final product happens to be one of an art or science which because of its very limitations can be clearly defined. In order to demonstrate the full measure of service that chemistry renders, one would have to show a cross section of all industry, a task manifestly impossible. On the other hand, it would seem practicable, if the physicists, chemists, and chemical engineers are really desirous of establishing themselves on a higher plane in public esteem, to assemble an exhibition or exposition of great popular appeal which would have a high educational value and, in addition, be an inspiration to all scientists. Especially would such an exposition be practicable were coöperation assured by all those engaged in industries that owe their existence to physicists and chemists.

There is hardly a single phase of American industrial or commercial activity which does not have its association. The Department of Commerce in "Commercial and Industrial Organizations of the United States" arranges the national and international organizations listed under one or another of seventy-one classifications. To research and development in chemistry and physics at least one-half of the industries so classified owe, if not their very existence, a large measure of the knowledge that makes them preëminent. There are no less than one hundred and nine societies or associations in the United States representing industries that are the product of the science of chemistry alone. Through the influence of chemists who are members of these organizations it should be possible to bring them all together for united effort in assembling an exposition such as is suggested. Among these organizations there are widely divergent interests and aims, but fundamentally all are the children of the science of chemistry. Probably the most logical body to take such a project in charge and to bring together all the different interests would be the Section of Chemical Education of the AMERICAN CHEMICAL SOCIETY.

There has been some criticism of the Ninth National Exposition of Chemical Industries, because it had little popular appeal and so enhanced the importance of the chemist but little in popular estimation. The critics lose sight of the fact that the exposition was made possible in large part by those desirous of establishing contact with prospective customers and that this purpose was served to the satisfaction of those most interested.

Consider the facts, because with facts before one, most problems answer themselves. If, as some critics contend, the chemist and the physicist are rated unfairly in popular esteem, is it because a perverse public refuses credit where credit is due, or, as seems more probable, because the exponents and practitioners of the twin sciences have encased themselves in cocoons of hieroglyph instead of spreading clear webs of expression to catch the popular imagination? When once the facts are understood and a sincere desire is awakened in each and every one concerned to correct the condition, then many opportunities will be found to establish the physicist and chemist on the plane to which they are entitled.

PAUL MC MICHAEL

NEW YORK CITY
October 15, 1923

The Fourth International Congress of Chemistry—Correction

In the article under this title [THIS JOURNAL, **15,** 1083 (1923)] under Section VIII, the conversion factor should read: 1 calorie 15° C. = 4.184 joules.

Determination of Ash, Arsenic, Copper, and Zinc in Gelatin

Editor of Industrial and Engineering Chemistry:

We have read with much interest, the article of Roger M. Mehurin, entitled "Determination of Ash, Arsenic, Copper, and Zinc in Gelatin" [This Journal, **15,** 942 (1923)]. As a result of the analyses in our laboratories of some ten thousand samples of gelatin during the past fifteen years, we do not feel that the conclusions of the author of the above-mentioned article are warranted.

In the first instance, the amount of sample to be taken for analysis as recommended by Mr. Mehurin—namely, 10 grams—is entirely inadequate for the accurate determination of the minute amounts of copper and zinc present in most samples on gelatin; and in many cases this also applies to the determination of arsenic. It follows, then, that on a suitably large sample, 50 to 100 grams, the ashing procedure is impractical. We have found from our experience that the methods as outlined by the Association of Official Agricultural Chemists, in *J. Assoc. Official Agr. Chem.*, **5,** 343 (1922), and revised to date by Claude R. Smith, of the Bureau of Chemistry, offer a simple, reliable, and accurate method of procedure for the determination of the above-mentioned impurities.

We have found that, if ordinary care in manipulation and proper technic are used, there is never any difficulty experienced in the saturation of the solution with hydrogen sulfide nor in its subsequent filtration.

Referring to the statement in the article by Mr. Mehurin, that "the determination of copper by titration with sodium thiosulfate is open to a considerable error because of the difficulty in obtaining a definite end point when small amounts of copper are titrated," we do not agree with the author in this respect. This objection has often been raised in our experience, and we have always been able to demonstrate that with proper technic it is possible to obtain end points which are sharp and remain so for half an hour or more. Furthermore, numerous blank and check determinations have shown conclusively that the method can be relied upon to give accurate results.

We have no criticism to make of the method for the determination of arsenic given by Mr. Mehurin, as we do not feel that there is any very essential difference between it and the A. O. A. C. method.

Irving Hochstadter

Hochstadter Laboratories
New York City
September 12, 1923

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Editor of Industrial and Engineering Chemistry:

Referring to Mr. Hochstadter's letter of September 12, published above, it will be noted that a 20 to 40-gram sample of gelatin, and not 10 grams, is specified for the determination of copper and zinc. In the tentative A. O. A. C. method referred to by Mr. Hochstadter, and of which he approves, practically the same range of sample is used—namely, 20 to 50 grams—and in the Hertwig method [*J. Assoc. Official Agr. Chem.*, **7,** 41 (1923)] a 20-gram sample is specified. No such range of sample as 50 to 100 grams is mentioned in any method for the analysis of gelatin and glue that has come to the attention of the writer. Since the metals are usually in solution with the gelatin during manufacture, they are uniformly distributed in the finished product and therefore as little as 20 grams of the mixed sample will usually be found sufficient.

A perfect ash will be obtained if the directions are followed, and as many as twenty samples can be added directly to a furnace 4 x $6^{1}/_{2}$ x 16 inches without previous charring and without requiring any attention whatever during the ashing process. From this point it has been the experience of the writer that an appreciable time is saved in handling small volumes of solution containing small amounts of inorganic salts rather than large volumes containing large amounts of organic material.

In regard to the copper determination, the writer has often experienced difficulty, as have others, in obtaining a definite end point when titrating very small amounts of copper with thiosulfate, and has obtained much more uniform results with the colorimetric method.

In conclusion, it may be stated that the method was not offered with any intention of supplanting or criticizing the accuracy of the tentative A. O. A. C. method (with the possible exception of the above-mentioned copper titration), but merely with the thought that it would be found to be less time-consuming in cases where it is necessary to analyze a large number of samples simultaneously. In this connection it may be mentioned that this method has been employed for some time past, in preference to all others, by the laboratory of one of the largest gelatin and glue works in the country.

R. M. Mehurin

Bureau of Animal Industry
Washington, D. C.
September 17, 1923

New Treatment for Gasoline

In his address before the Mid-West Section of the Society of Automotive Engineers in Chicago, October 12, C. F. Kettering, president of the General Motors Chemical Company, announced that this company and the Standard Oil Company (Indiana) had entered into a contract for the distribution of ethyl fluid.

Ethyl fluid is the new addition agent for gasoline, and has the effect of increasing engine efficiency and taking the knock out of an engine, no matter under what conditions or load an automobile is driven. It is the result of several years' research and test at the laboratories of the General Motors Research Corporation in Dayton, and has met with enthusiastic reception from motorists in Dayton and in Cincinnati, Ohio, where it has been placed on sale at a few stations.

Gasoline treated with ethyl fluid has a characteristic light wine color, which distinguishes it from other automobile fuels.

Distribution by the Standard Oil Company (Indiana) will cover the States of Indiana, Michigan, Illinois, Minnesota, Wisconsin, Iowa, Missouri, Kansas, South Dakota, and North Dakota as soon as installation can be made. The southern part of the distributing territory is being equipped this winter and the northern part will be equipped as early as possible in the spring, in order that motorists may be supplied when the 1924 motoring season opens. It is believed that all the Indiana company service stations will be open and ready to supply the treated fuel by July 1, 1924.

Dictionary of Specifications

The work which the Bureau of Standards is carrying out on a dictionary of specifications has made good progress. During the past month existing specifications have been collected from more than 75 per cent of the important national technical societies, trade associations, and governmental publishing agencies that have issued specifications. Leaving out all duplications, it would appear that about 5000 specifications are available from these sources. However, not all of these specifications can properly be classed as related to commodities purchased by the Federal, State, and Municipal Governments and public institutions. It is believed that about 20,000 commodities do come within this class and of these more than 75 per cent of all commodities purchased for Government consumption are not covered by available specifications.

Work is being expedited on the collection of existing specifications with the object of making the collection as complete as possible so that the first step in the preparation of the dictionary, the issuance of a classified list of existing specifications, may soon be taken. This will be of considerable service to all agencies interested in this subject, and with the coöperation of the advisory board will be used as the basis for selection of specifications for inclusion in the dictionary.

WASHINGTON NOTES

Keen Interest in Chemistry

If the first meeting of the Local Section, which was held at the Cosmos Club on the evening of October 11, can be taken as a criterion of what is to follow, the coming winter may easily become a record one so far as things chemical are concerned. Over one hundred and sixty chemists were present, thus making the meeting one of the best attended in the history of the section. E. W. Washburn was the speaker of the evening, lecturing on "Physical Chemistry and Ceramics." After his address the meeting was turned into an informal reception to the following prominent chemists who have recently cast their lot with us: C. A. Browne, newly appointed Chief of the Bureau of Chemistry; George L. Coyle, who has come to Washington to head the Chemical Department at Georgetown University; S. C. Lind, chief chemist of the Bureau of Mines; J. E. Zanetti, chief of the Division of Chemistry and Chemical Technology of the National Research Council; and C. S. Hudson, who has returned to Washington after an absence of several years and is now connected with the Bureau of Standards.

As a further evidence of the steadily growing interest in chemistry, may be mentioned the following addresses before the Women's City Club on the evening of October 10: "The Romance of Chemistry," by H. E. Howe; "The Chemistry of Food," by W. W. Skinner; and "Chemistry in Business," by F. B. Gorin. Again, on the evening of October 17, L. I. Shaw, of the Bureau of Mines, addressed the Piney Branch Citizens Association, choosing "Helium" as his subject.

Alcohol Trades Advisory Committee Issues Report

The proposal to create a separate bureau of government for the enforcement of prohibition, independent of departmental control and answerable only to the President, is condemned in a report submitted to the Bureau of Internal Revenue by its Alcohol Trades Advisory Committee, composed of eleven representatives of scientific societies and industries in which alcohol is an indispensable chemical raw material. The committee claims that such a procedure would be contrary to long-established practice under our system of government and that it would seriously handicap scientific research and lawful industry. The committee showed that a similar scheme was incorporated in the Ernst-Wood Bill (H. R. 12035–S. 3713), introduced in the last Congress, which was opposed by all scientific bodies and legitimate trades and failed to be even reported by the House Judiciary Committee after an open hearing. They add that "the proponents of such a bureaucracy may be assured that it will be opposed with every ounce of energy that can be put forward by those engaged in lawful professions and businesses in which the chemical alcohol is required and used."

The report points out that in the World War the production of nonbeverage alcohol was rated as one of the nation's "key industries" and "is admittedly a basic chemical essential to our national defense, industrial and economic development, and even to the advancement of civilization itself." A comprehensive chart and other data showing the innumerable scientific and industrial uses of alcohol are appended to the report. It asks "from where is the essential future supply of alcohol for governmental, industrial, and scientific purposes to come? Under present conditions of prohibition law enforcement we have real cause to be concerned."

The committee characterizes the attacks upon the Secretary of the Treasury and the Commissioner of Internal Revenue as being as unfair as unwarranted, both of those officials having but properly and justly exercised their statutory right of review. It states that the action of the Government in placing in the hands of a Prohibition Commissioner without essential technical and economic training the duties of carrying out the Congressional mandate to promote the use of alcohol in scientific research and development of lawful industries, was illegal by implication, illogical by any method of sound reasoning, economically impracticable, and should be forthwith corrected. The committee recommends that the Commissioner of Internal Revenue designate a deputy commissioner or appoint an industrial alcohol commissioner to take over the administration of that phase of the law. In this way, they claim, efficient and scientific administration would be assured and at the same time the Prohibition Commissioner would be relieved from routine work incidental to serving legitimate industry and could devote the necessary time to his logical police duties. The committee states, "we yield to no one in our adherence to the principle of law enforcement, but surely the National Prohibition Act can be so administered as not to interfere with the health, economic needs, and the national defense of the country."

Tariff Commission Hearings

Final argument on the application of coated paper manufacturers for a 50 per cent reduction in the present duty of 2.5 cents per pound on casein was heard on September 25. Henry A. Wise appeared as counsel for the consumers of between 75 and 85 per cent of the casein used in this country, and argued for a lower tariff rate, declaring that casein was absolutely necessary to the coated paper industry since domestic production had never been adequate.

The hearing on rare sugars and amino acids, scheduled for September 27, was adjourned because no witnesses appeared.

On October 6 final arguments were presented for an increase of 50 per cent in the duty of 3 cents per pound on sodium nitrite. No facts relative to costs of production were presented, but the greater part of the time was consumed by an argument by former Senator McCumber, attorney for the American Nitrogen Products Company, and joint author with former Representative Fordney of the 1922 Tariff Act, on the procedure to be followed by the Tariff Commission. Mr. McCumber argued that the commission has no authority to recommend conclusions to the President, but must confine its duties to investigations and the submission of reports based on field work and hearings; that the President is not bound to accept the findings of the commission, but may call upon any other agency for additional reports or advice; and that witnesses at public hearings should not be cross-examined by any one except the commissioners.

Other hearings of interest to chemists and thus far announced by the commission are: Oxalic acid, November 5; diethylbarbituric acid and its derivatives, November 7; barium dioxide, November 9; logwood extract, November 12; potassium chlorate, November 14; and sugar, January 15, 1924. In connection with the last-named hearing, the commission has announced a new policy in that on or about December 1 it will make available to interested parties a statement of the data secured on costs of production in the pending sugar investigation, as well as a statement of basic points and problems, as, for instance, the rate of interest allowed by the commission, depreciation allowances, etc.

Forest Service Expands

Two new experiment stations have been established under the provisions of the appropriations for the Forest Service made at the last session of Congress. One of these, the Northeastern Experiment Station, will have headquarters at Amherst, Mass., and operate in conjunction with the Massachusetts Agricultural College. The other one, the Lake States Forest Experiment Station, will have its headquarters at St. Paul, Minn., under a coöperative arrangement with the Minnesota Agricultural College. The establishment of these stations is in conformity with the program of the Department of Agriculture whereby each important forest region will be supplied with a station to handle local forest problems. It is expected that the forest experiment stations will aid the progress of forestry as much as the agricultural experiment stations have aided the progress of agriculture. S. T. Dana, formerly Forest Commissioner of Maine, has been appointed director of the Northeastern Station, and Walter H. Meyer, assistant. Raphael Zon will be the director of the Lake States Station.

National Research Council Endorses Prize Essay Contest

The Interim Committee of the National Research Council at its meeting on October 17 adopted the following resolution upon recommendation from the Division of Chemistry and Chemical Technology:

> Whereas, The encouragement of the study of chemistry among high school students is of great importance in stimulating scientific interest among the generation which will later supply research workers in science, therefore, be it
>
> *Resolved*, That the National Research Council considers the purpose of the Prize Essay Contest established by the American Chemical Society under the grant made by Mr. and Mrs. Francis P. Garvan as worthy of encouragement and approval.

Enforcement of the Naval Stores Act

The Bureau of Chemistry has distributed to the trade press, producers, factors, dealers, and users of turpentine and rosin, a tentative draft of proposed regulations for the enforcement of the Naval Stores Act of March 3, 1923. Twenty such regulations have been drafted and they are submitted for consideration and to permit those who desire to offer suggestions for amendment. Suggestions for amendment or requests for further information should be addressed to the Acting Chief of the Bureau of Chemistry, Washington, D. C.

Should the suggestions for amendment warrant, a date will be set for a public hearing at which any interested party will have an opportunity to advance arguments for proposed changes. Should no material amendments be suggested, however, it is probable that the regulations will be issued in approximately their present form, if and when approved by the Secretary of Agriculture.

Meanwhile, the Bureau of Chemistry is carrying on naval stores demonstration work in the South. The purpose of this work is to offer to individual producers of rosin and turpentine, through visits to stills by a practical operator of good judgment, information as to the most practicable and profitable methods for the production of naval stores, and to aid them in solving technical problems involved in the manufacture of these commodities. It is believed that this work will aid the producers in complying with the act.

Forestry Advisory Committee

Twenty leaders in the American pulp and paper industry have been asked by Secretary of Agriculture Wallace to form an advisory committee to work with the Department of Agriculture in formulating and carrying out its forestry policies which relate to the supply and use of timber in making paper and kindred products. It is thought that the creation of an advisory committee of men intimately concerned with the pulp and paper industry will be beneficial in dealing in a searching way with the fundamental problems of the industry.

October 22, 1923

PARIS LETTER

By **Charles Lormand**, 4 Avenue de l'Observatoire, Paris, France

Effect of Japanese Earthquake

The earthquake which devastated Japan has affected the market of chemicals in France. In the days which followed the announcement of the catastrophe, camphor, menthol, and oil of peppermint doubled in price. The celluloid industries were afraid that they would not be able to supply themselves, and the synthetic camphor factories, which are rivals of those of natural camphor, considered equipping themselves to increase their production.

When more circumstantial evidence was obtained, it was perceived that speculation alone had caused the rise in price since the camphor plantations are in Formosa and the market center at Kobe, far enough away from the stricken region so that the production of camphor could not be injured.

National Fuel

The decree obliging importers of oil to buy a corresponding amount of alcohol to constitute the national fuel is being vigorously enforced. It has been decided that in the interests of the development of the consumption of the national fuel, absolute freedom as to the price of oil and alcohol would be given to the manufacturers and importers. Contrary to expectations the minimum selling price has not been regulated.

In connection with this question of national fuel, it has been necessary to study the means of preservation of the alcohol or the alcohol-oil mixture. Preservation in tanks of great volume necessitate the dehydration of the air in the tanks. In fact, in damp climates atmosphere saturated with water vapor soon increases the water in the alcohol-oil mixture. The variations of temperature of this more or less humid air change the proportion of concentration of the alcohol or the stability of the alcohol-oil mixture.

To solve this problem, M. Dumanois proposes the addition of a small auxiliary reservoir to the large storage reservoir. This reservoir contains a large number of baffles and is filled with alcohol at 95° C. All the manipulations of the liquid in the reservoir cause the air to enter or leave through this smaller reservoir. The alcohol which it contains absorbs the water vapor of the air when the air is exhausted. Under these conditions only the dehydrated air can enter the large reservoir.

Fertilizer

It is well known that more nitrogen is used in the nitric form than in the ammoniacal form, but a satisfactory explanation to this phenomenon has not been given. It is estimated at present that the ammoniacal salts cause in the plant an acid secretion which is harmful to its development. By avoiding this secondary action by some means, with ammoniacal compounds a product always identical, sometimes superior, to that obtained by the nitrates would be obtained. The use of calcium salts, especially the carbonate and the sulfate, with the ammoniacal salts would permit these results to be obtained.

Czechoslovakia is developing considerably its agricultural industries and is therefore consuming increasing quantities of fertilizer. MM. Jahn and Prikes have carefully examined the Czechoslovakian soil, and have succeeded in finding new deposits of potash. These deposits are estimated at 70 million tons as a minimum. They are particularly interesting for this country where the cultivation of the beet is extensive.

Moreover, the Czechoslovakian industries have just opened up at Prague an Experimental Institute of the Sugar Industry. This institute is divided into five sections: (1) Chemical Section, (2) Beet Section, (3) Physico-chemical Section, (4) Section of Hygiene of the Beet, (5) Machines Section. The originality of this unique institute devoted to the study of the beet and to the manufacture of the sugar consists in the fact that it is organized to receive technicians or chemists of other countries who desire to go there to study the latest methods of work accomplished at the institute.

Scientific Congresses

Two important Congresses have been held—one at Strassburg, and the other at Bologna.

The Congress at Strassburg was held with the Pasteur Exposition and had for its object the study of refrigeration from the point of view of production and utilization. Of particular note were the explanations that were given to the utilization of freezing in the preparation of vaccines and in medicine. It was pointed out that it could be used advantageously to replace X-rays or radium in the treatment of cancer and tumors. Here is a field of unexplored work.

There was also proposed a means of using low and constant temperatures in research laboratories. Without descending to temperatures as low as those of liquid air, it is certain that in the investigations of temperatures between 0° and −50° C., the chemical reactions and phenomena are not sufficiently known and merit further study.

At Bologna was held the Fish Congress, destined to extend the use of this food. From the chemical point of view different interesting questions were taken up, especially the relations between the saltiness of the ocean and the migrations of fish beds, and, finally, on the chemical properties of fish oils, notably from the point of view of their richness in vitamins. The value of certain oils, especially the oil of cod liver, is attributed to their richness in vitamins, and it seems to be quite certain that the ocean is a medium particularly rich in all sorts of vitamins.

Along the same line, Mme. Randoin has recently pointed out that the source most rich in vitamins is the oyster. It is the antiscorbutic vitamin which the oyster contains in the proper proportions that has never been found before in a single living organism. The oyster could be a source of vitamins, not only for consumption, but to facilitate the investigations on their isolation.

Death of M. Violle

M. Violle, dean of the Section of Physics of l'Académie des Sciences, has recently died. M. Violle studied the problems of radiation of bodies at high temperature. To him we owe the establishment, in 1884, of an absolute standard of light given out by a unit of surface of melted platinum, a standard which is universally recognized under the name Violle.

October 5, 1923

LONDON LETTER

By Hugh Griffiths, 15 New Bridge Street, London, E. C. 4., England

Key Industries Act

The unsatisfactory nature of the operation of the Key Industries Act is clearly exemplified by the decisions made in two recent cases. It has been decided by the referee that formaldehyde cannot be considered as a fine chemical, and it has accordingly been removed from the list of materials subject to duty. On the other hand, Rochelle salt is held to be a fine chemical, and is to be retained in the list.

These decisions, when all the evidence is read, sound to be fairly reasonable, but those familiar with the chemical trade will have a very natural feeling that there is something conflicting in the position which has resulted. A movement is afoot to get the whole basis of this act altered.

Resignation of A. G. Green

A mild sensation has been caused by the resignation of A. G. Green from his position as director of research to the British Dyestuffs Corporation. It will be recalled that not very long ago two of the technical directors resigned. From the statements which have been made it seems pretty clear that the business men in this organization do not see eye to eye with the technical staff on the subject of expenditure on research, and while, on the one side, it is urged that the organization cannot support a very expensive research department, it is equally urged on the other side that unless the research proceeds the company cannot maintain its position.

This difficulty is one which is very common in this country at the present time, and although perhaps research work is now receiving more support than ever before, there is a feeling that business depression is making firms niggardly, and the only research which receives anything but the most grudging support is of a purely hand-to-mouth character, and investigations of fundamental matters are being left more and more to academic institutions. It must, however, be admitted that at the present time, when most chemical works in this country are feeling the effects of depressed trade, the cost of research organizations may eat up a large proportion of the gross profit. The only solution would appear to be to take a leaf from our neighbors—namely, in subsidizing research from the pocket of the taxpayer.

New Plant Equipment

At the Ship Building and Engineering Exhibition, the new stream-line filter is being demonstrated. In its simplest form this filter consists of a pack of paper sheets held together between distributing heads. The pack is perforated by a large number of holes. About half of the passages so formed are connected at one end to the feed chest in the lead of the press, and the remainder to the filtrate outlet chamber.

The filtration takes place at the edges of the paper sheets. It is stated that the paper employed is waterproof, that the apparatus therefore does not depend upon the porosity of the paper, and that the only apertures for filtration to take place are formed by the spaces between the sheets due to roughness.

When the apparatus was first described by Hele Shaw, it was thought that perhaps there would be difficulties in discharging the solids, but a very simple device has been applied to these presses, the tubular collecting spaces being fitted with small plugs which can be operated by the feed pressure to the filter. In a horizontal press it is consequently possible to discharge the deposited solids by the manipulation of valves, which cause the plugs to travel under the fluid pressure in either direction, so expelling the solid. It is stated that in many cases a fairly dry solid material can be obtained which is extruded from the apparatus as a continuous rod.

The most interesting feature of this apparatus is that most extraordinary claims are made regarding its efficiency as an ultra-filter. A solution of an organic dyestuff such as erythrosin can be passed through the press when the filtrate emerges absolutely colorless. This extraordinary result is stated not to be due to adsorption, and it is claimed that the feeding of the erythrosin solution can be continued without getting a colored filtrate. It is also claimed that when brine is passed through the apparatus a considerable proportion of the water can be separated from the salt, and it is stated that in this case the effect is not merely one of adsorption, but the salt is actually filtered out from the water. On theoretical grounds one would have thought that this would be impossible, as a system of apertures sufficiently fine selectively to separate molecules of different sizes would be expected to render liquid flow almost impossible. It is suggested, however, that possibly salt forms some sort of hydrate complex with water, which makes this separation possible. It is, however, very extraordinary that salt will pass through a dialyzer such as the well-known osmogene, if simple filtration will effect a separation.

Apart from this astounding result, the apparatus would appear to have attractive possibilities for fine filtration work, and the compactness of construction is an attractive feature. A comparatively small and insignificant looking press is stated to be capable of filtration at the rate of 250 gallons per hour on a simple water solution, and owing to the small diameter of the passages employed the depth of the deposited layer of material is small, and consequently the effect of the thickness of deposit is not quite so great as in an ordinary filter press.

Some installations of this type, of considerable size, are at present under construction, and the results of these larger installations will be waited for with the greatest interest. This filter is reminiscent of the Plauson filter, but is very much cheaper in first cost, and only resembles the Plauson filter in having a laminated filtering medium.

A new mill, known as the premier mill, has recently appeared, which is used for mixing, emulsifying, and very fine disintegration. In its application this machine resembles to some extent the colloid mill, but it is explained that the operation of this new machine depends simply upon hydraulic shear. In principle the mill consists of a conical seating in which a conical rotor revolves at a very high speed, the clearance between the two conical surfaces being very accurately adjustable.

If a mixture of a liquid and a solid can be passed into this machine, the action of the shearing forces due to viscosity as the liquid passes between the working surfaces serves to produce the desired effect. This machine has already received a number of important industrial applications, not merely for disintegration purposes, but for securing contact between immiscible liquids in the preparation of emulsions, and for similar work. The machine is very well constructed, and not too expensive.

The vacuum drying machinery used in this country is substantially unaltered in design since before the war. From time to time, however, suggestions come forward in connection with the condensing part of the operation, but in the past nothing has been found which would compete with the ordinary vacuum pump for the production of the vacuum.

Recently in this country there has been a tendency in power plants to employ steam ejectors for maintaining vacuum, and it is not surprising that the suggestion to apply these to vacuum drying and evaporating plants should arise. In the past the claims made by the makers of steam ejectors for vacuum production have been decidedly modest, and when one examines the figures given for steam consumption, and bears in mind the instability of such appliances against fluctuating duties, he is perhaps not surprised that the vacuum pump has always managed to hold its own.

An English firm has now commenced to manufacture a vacuum drying plant in which the vacuum is produced by a two-stage steam ejector of the Delas type, having water-jacketed diffusers. It is suggested that the exhaust steam from the ejector can be used for heating the vacuum drier, and it is stated that this system has been in use in France with excellent results.

This proposal is not new, for in the past similar schemes have been tried, but they have invariably been proved to be unreliable. In the case of the plant now under notice, it appears that the superiority claimed depends upon the use of the special type of ejector employed, and the statement has been published that, even though the steam supply to the ejector should fluctuate in pressure over very considerable limits, the performance is still satisfactory.

Much more interesting, however, is the experimental work which has been carried out by a large chemical firm in this country on the methods of producing vacuum in distilling plants for corrosive liquids. Some very excellent work in this direction has been done, using an apparatus very similar in principle to that of Siepermann. This apparatus is a sort of reversed air-lift pump in which the air is removed by means of a full tube something after the fashion of the Taylor hydraulic compressor.

This apparatus has no moving parts, and the working fluid in the pump may consist of the liquid which has to be finally condensed. The mechanical efficiency is not very high, but the wear and tear is negligible, and there is absolutely nothing to go wrong. It would not, however, be suitable for ordinary vacuum work, as the cost of running would be higher than that of ordinary vacuum pump, but where corrosive materials have to be handled the scheme seems to be very attractive.

Cotterill Plant Interferes with Radio

A strange complaint has been heard from radio enthusiasts in the north of England. It appears that a certain Cotterill dust-collecting plant creates a nuisance and effectually jams out broadcast wireless communications. It is understood that this matter is at present under investigation, but the plant in question emits the disturbance on a wave length of about 450 meters, with the result that tuning out is very difficult. This matter is rather interesting from a legal point of view, but it is difficult to believe that the trouble can be any worse than that created by electric trains, except that of course it will be continuous, and there can be no doubt that something will ultimately be done to abate the trouble.

September 11, 1923

GERMAN LETTER

By Walter Roth, Göthen, Germany

Training in Industrial Chemistry

Recently in Germany there has been a revival of interest in the problem of training the chemist. During the war experience was the most important, so that in technical circles the necessary industrial education was lacking. Now, therefore, there comes more than ever the demand for the industrial point of view, the consideration of the economic aspects of the problem. A new branch of chemistry, industrial chemistry, will fill this gap in the education of the chemist, by training him along economic lines. For, today, in order to carry out a large chemical undertaking a mere knowledge of the subject is not sufficient; questions of procuring raw materials, or the possibilities for revenue of a process, and world economic problems must be solved, and for this a broader, industrially experienced point of view is needed.

New Materials for Fuel and Power

In the present fuel famine one naturally turns his attention to other sources of energy besides coal and lignite. But the "white coal" will for Germany, who is poor in water power, never be able to play a large part. Still less is to be expected of the "blue coal"—the using of the tide, by its ebb and flow—for German industry; and the large-scale utilization of the other forms of energy of earth and space—wind, sun, atmospheric electricity, etc.—are still in the distant future. Successful attempts have been made here and there to turn sewage and settling plants to purposes of light and power. For example, the City of Erfurt, in Thüringen, by experiments of the Erfurter Trichter Gesellschaft, has obtained out of a total quantity of 4000 cc. of mud, over 1,000,000 cc. of gas (marsh gas), and turned this to profitable use.

Direct Utilization of Rubber Latex

It is well known that the milky juice of rubber, the so-called latex, is used directly, without first separating the rubber—for example, for the making of cord thread, of latex paper, etc. According to Ditmar it is suitable only where the latex can be given the form of the desired rubber article under simultaneous dehydration. When cement or plaster of Paris is used as the hardening agent, then vulcanization is not needed as these dehydrating agents act at the same time as vulcanizers. Through treatment with latex Ditmar will produce mothproof, elastic cushion and mattress fillings, since the loosened filling in the natural or pasteurized latex is wet and then left to dry off from the excess milky juice. The materials are thus covered with rubber, and therefore are mothproof, as rubber is not attacked by moths. This coating with rubber Ditmar calls "latexing," or after his own name, "ditmarizing." Ditmar will also use latex as a cementing material. He recommends latex glue, especially for the waterproof cementing of panes into windows.

Chromium Instead of Nickel Plating

The Electrochromgesellschaft, in Berlin, jointly with the Langbein-Pfanhauser Werken A. G., Leipzig, is using a new galvanic process by which coatings of chromium are made. Metallic chromium is separated electrolytically from chromium solutions in a form capable of being polished. These are platinum-colored, heat-resisting coatings, which are especially distinguished through their great hardness. They can be much thinner than nickel coatings, and are little attacked by the atmosphere, alkalies, acids, or salts. Especially can medical instruments, typewriter parts, phonograph plates, burners, lighters, valves, etc., export articles with shining surfaces, which will not stand overseas transportation, be plated with chromium.

Dust Explosions

In mills, sugar factories, soap factories, etc., many dust explosions have been experienced without any one being able to find their cause. In sugar factories alone in the last thirty years almost seventy such explosions have taken place. In the Frankenthal plant the sugar chemist, Beyersdorfer, has been experimenting for a year and has found out that most explosions of this kind can be traced to electric causes. The dust explosions are to a certain extent "dust storms" by which the incipient lightning ignites the clouds of dust and causes them to explode. Beyersdorfer calls technical dust of this kind "colloid-chemical," and sees no difference between suspended dust, smoke, and clouds.

In this connection, he explains the rain of fire of Sodom and Gomorrah in a similar way. He says that with a violent outbreak of a petroleum well, perhaps in the Caucasus, followed by scattering and electrical charging of the liquid petroleum by the eruption out of a fissure in the earth, a petroleum cloud was formed. This cloud was then driven to Sodom and Gomorrah; there the oil was ignited by a flash of lightning and fell down as burning petroleum rain. Beyersdorfer rightly considered it fortunate that the particles of the clouds separated by the lightning in ordinary storms do not consist of combustible material; otherwise every storm would be a rain of fire

For the prevention of dust explosions Beyersdorfer recommends limiting the formation of the dust as much as possible through the choice of appropriate disintegrating machines, not to grind too fine, to wet down the dust with water, and to remove the electrical charges through contact with the earth or through electrical neutralization.

Methane in Steel Containers

Methane from the Rombacher mines in Coblenz and from the Fritz Hamm Gesellschaft in Dusseldorf, compressed in the usual steel containers to 150 atmospheres, has recently been put on the market. This methane is entirely free from carbon monoxide, and is said to be generally useful as a cooking and lighting gas where a connection to a gas plant is not convenient or possible—as, for example, on ships, in remote villages, hamlets, and in factories situated far from the city. Methane light is pure white. Methane is suitable for soldering purposes, for the autogenic working of copper, brass, aluminium, and similar easily melted metals, as well as the autogenic cutting of iron. On account of its high calorific value and its extremely favorable kindling and compression points, methane is also useful as a material for gas motors, especially for vehicles. In the chemical use of methane, and therefore of natural gas, of which methane is the chief constituent, many prospects offer themselves. It is planned to obtain sulfur from gypsum by reduction with methane, to produce methanol from methane, with methyl chloride as an intermediate product, and from atmospheric nitrogen by the use of methane or its cleavage products to prepare cyanogen products. As is well known, methane decomposes at temperatures over 1000° C. into hydrogen and carbon. If, now, this very pure carbon is mixed with barium carbonate, or briquets are formed from the mixture, and these are heated in a stream of nitrogen at 1100° to 1300° C., barium cyanide is obtained. This new process of Prince Carl Löwenstein and Dr. Hauff makes possible the production of an air-nitrogen industry in the vicinity of natural gas sources.

August 23, 1923

BOOK REVIEWS

Surface Tension and Surface Energy and Their Influence on Chemical Phenomena. By R. S. Willows, M.A., D.Sc., and E. Hatschek. 3rd edition, revised by R. S. Willows. viii + 134 pages. 25 illustrations. P. Blakiston's Son & Co., Philadelphia, 1923. Price, $2.00.

The owners of previous editions of this compact and convenient little treatise on a subject so closely connected with the important fields of colloid chemistry, adsorption, and catalysis will welcome this revised edition. The revision has consisted mainly in the enlargement of the text so as to include the recent work on the properties of thin films, surface solutions, boundary lubrication, and the relation between surface phenomena and the recent theories of molecular and atomic structure. Numerous other small additions and changes in other portions of the text have also been made to bring it up to date. The unnecessarily long and involved derivation of the Gibbs adsorption formula, given in the appendix, ought to be replaced by a shorter derivation of the rigorously exact equation which can be obtained directly from the Second Law. The assumptions necessary to convert the exact formula into the customary form can then be clearly brought out. These assumptions are not those indicated by the authors on p. 79, *et sec.*

E. W. Washburn

Metals and Metallic Compounds. By Ulick R. Evans, M.A. 22.5 × 15 cm. Longmans, Green & Co., New York; Edward Arnold & Co., London, 1923. **Vol. I,** xii + 468 pages. Price $7.00. **Vol. II,** xi + 396 pages. Price, $6.00. **Vol. III,** xii + 270 pages. Price, $4.75. **Vol. IV,** xii + 350 pages. Price, $6.00.

This work is in reality an advanced text or handbook dealing with the chemistry of the metallic elements only. "The book is intended for the advanced student of inorganic and metallurgical chemistry and for those engaged in research in these subjects."

The first volume is of a general character and the first 120 pages are given to a presentation of the principles of general chemistry, physics, and geology. The contents of the main part of this volume is classified under two general headings, metallography and electrochemistry. The metallographic portion includes discussions of the structure of simple metals, the effects of deformation, and the effect of annealing and alloying on the properties of metals and the structure of alloys. Under the heading of electrochemistry are included chapters on such subjects as the structure of precipitates, the colloidal state, electrodeposition and corrosion, and electrolytic valve action. The volume is concluded with a chapter on radioactivity. This volume contains a wealth of material which should prove of interest to even the most advanced student of inorganic chemistry.

The remaining three volumes of the work are devoted to a consideration of the individual metals. Volume II deals with those elements classed as "A" groups, according to the periodic table of Sir James Walker, and includes the alkali and alkaline earth metals, aluminium and the rare earths, tantalum, columbium, and the chromium group. The space devoted to each metal is divided into three sections, the first dealing with the metal and its compounds, the second with the occurrence of the metal—including a discussion of its origin and formation of its compounds from the standpoint of geology, the third dealing with the technology of the element or of such of its compounds as are of commercial importance.

Volume III deals with the transition elements—that is, the platinum and iron groups. The element iron is treated in a very comprehensive manner, 125 pages being devoted to it. The metallurgy of iron and the manufacture of common and alloy steels are presented in considerable detail.

Volume IV deals with the remaining metallic elements or the metals of the "B" groups, and includes arsenic and antimony.

In preparing this work the author has taken full advantage of the results obtained by research workers during the last few years to round out the presentation of the various subjects and bring the books up to date. As a result these books contain many subjects, presented in considerable detail, which are not now ordinarily found in books of this type. The books are unusually well written in a readable style and in the opinion of the reviewer are well worthy a careful perusal, particularly by advanced students or research workers in the fields of inorganic or metallurgical chemistry.

C. W. Balke

Industrial Filtration. By Arthur Wright. 336 pages. Chemical Catalog Co., Inc., New York. Price, $5.00.

By definition of the title this book does not consider municipal water filtration, boiler water filtration, etc.

Part I, entitled "Theory of Filtration," might better be called "Art of Filtration," as no theoretical considerations as generally understood are made. It deals with clarification, cake, building, washing, discharging, filter media, theory (art?) of filter application and auxiliary equipment. It is fairly well written but lacks in specific information. Under "Cake Filtration" the methods used to determine the economical limit curve are questionable. The data are apparently not obtained by the best methods, and the conclusions are doubtful and certainly not applicable to the most commonly used filters. Under "Cake Washing" is given the usual misleading curve, which has appeared in print so many times, comparing simple washing in leaf filters with thorough washing in plate filters. If simple washing were used in both cases the curves would be quite alike. The impression is given that simple or displacement washing cannot readily be used in ordinary plate filters; whereas, as a matter of fact, it is used to a considerable extent. Thorough or alternate plate washing is a satisfactory method of washing, despite the author's impressions to the contrary. Under "Theory of Filter Application" the applications assigned to the five types are incomplete and hardly sufficient to effect a choice. "Auxiliary Equipment" is treated too briefly; it does not mention the montejus and gives too little attention to steam or power pumps or pump valves. There is nothing specific about the materials of which pumps should be made for use with various liquors.

Part II, "Mechanics of Filtration," might more understandably be called "Filtering Machines." Plate and frame filter presses are not handled well. Misstatements are made, producing a wrong impression of this most important filter of today. The rest of the section deals with suction, leaf, and vacuum filters. More space is devoted to these machines than their actual use in industry seems to warrant. A few other special filters of little importance are described. No description is given of the Berrigan, centrifugal, or pulp filters, although considerable space is given to thickeners, which are not filters at all.

Part III, "Filter Practice," gives general information of more or less value.

In general, the book contains a good description of the mechanics and operation of leaf or vacuum filters, and certain filtration ideas of value are advanced. Like many "technical" books, however, it lacks specific information. No cost data are given, and a list of the rates of flow of the common important substances is missing. Weights of various filters are also absent. The layout information is rather too brief and very few sketches appear. The average reader with a specific problem to solve would not be able to determine properly the type, size, or cost of filter to use from the information given.

It is unfortunate that the author mentions the names of certain manufacturers of equipment so frequently while names of others in the same line are not mentioned.

This book can be said to be equally as good as other books on this subject and represents an effort to produce a book which is much needed.

D. R. Sperry

The Chemical Engineering Catalog. 8th Annual Edition. Francis M. Turner, Jr., Technical Editor. 1049 pages, tables, diagrams, and illustrations. The Chemical Catalog Co., Inc., New York, 1923. Price, $10.00. Leasing fee, $2.00 ($3.50 foreign).

So firmly established has the Chemical Engineering Catalog become as an institution in the chemical industries, that it would be almost unnecessary to comment on its annual appearance but for the fact that each succeeding edition shows plainly the result of the efforts being put forth by the supervising committee and the publishers to improve this standard reference work. In the earlier editions a great deal of material appeared which really partook more of the nature of advertising than of the type of data one might reasonably expect in a system of condensed catalogs. It was only natural that at first there should be a certain amount of confusion between this publication and various directories containing advertising that had appeared unofficially in other technical industries. However, year by year, more and more manufacturers of equipment have taken the trouble to study the requirements of those in charge of our chemical industries, and the present edition of the Chemical Engineering Catalog reflects this tendency.

It is particularly gratifying to note the much greater use of really explanatory diagrams and charts. There also seems to be an increase in the number of concerns giving detailed information as to sizes and capacities. There is still a dearth of information as to the costs of various equipment and materials. It would seem that approximate costs could be furnished in such a work where it is not possible to give exact figures.

The Equipment Section occupies the bulk of the book. The Chemicals and Materials Section is greatly improved and many of the larger manufacturers of chemicals are giving really detailed specifications of their products. However, there still remain in this section many pages which are mere lists of chemicals and other materials. Such pages certainly supply little information to prospective buyers, and in the case of a choice the business goes to the firm supplying the more detailed information.

A somewhat definite policy from previous years has been adopted with regard to the listings in the classified index at the front of the volume. Firms not coöperating in the catalog are now listed only in cases where they are not manufacturers of such products represented in the volume. This seems an entirely fair and satisfactory arrangement. It guarantees a complete reference work to the users of the catalog, and it relieves those who are coöperating in the support of the publication from the competition of firms contributing nothing to its support. Moreover, as the great majority of leading manufacturers are represented in the catalog, there are only relatively few instances where it is necessary to apply this rule.

The Technical and Scientific Book Section is considerably enlarged, and is interesting as being the only complete, up-to-date bibliography of technical books in English dealing with chemistry and closely allied subjects.

The quality of the paper and presswork seems to be even better than usual, and the general appearance of the volume conforms to the high standard established by previous editions.

Chemische Technologie des Steinkohlenteers. By R. Weissgerber. 141 pages. Otto Spamer, Leipzig, 1923. Price, $1.50.

This monograph is a worthy member of the chemical technological series founded by Ferd. Fischer and edited by Arthur Binz. The subject matter, arranged in two main divisions, coking and coal tar, gives a concise and remarkably clear presentation of the most salient features, both theoretical and practical, of an industry in which the author is a recognized authority. The first division occupies thirty pages and deals with the various types of coal, their nature and probable formation, more particularly their behavior under destructive distillation in both low- and high-temperature operations, and the technic and chemistry of the resulting products. The remaining pages constitute the second division, coal tar, and deal with material derived exclusively from distillations at temperatures above 700° C. (high-temperature coking). Here the treatment is more elaborate, following the subdivisions: Theory of Tar Formation, Properties, Classification and Statistics, Tar Analysis, Transport and Storage, Tar Distillation, Light, Medium and Heavy Oils, Anthracene Oil, and Pitch. In addition to numerous references to pertinent literature, the book is well illustrated with up-to-date ovens, retorts, and apparatus peculiar to the industry, and is therefore well worth the attention of every progressive coal-tar technologist.

W. O. Emery

Betriebsverrechnung in der Chemischen Grossindustrie. By Albert Hempelmann. vi + 107 pages. Julius Springer, Berlin, 1922. Price, $1.15 unbound; $1.40 bound.

Cost accounting in the chemical industry, with which this pamphlet deals, is of increasing importance to the works and managing chemist or engineer.

This work is comparatively brief and general in its treatment. It leans to the economist's or financial point of view rather than that of the production manager. The work is divided into six parts, with many sections and subdivisions. The main sections take up such subjects as the foundations of cost systems in the chemical industry, raw materials' cost, operating cost, calculation, calculation methods, detailed relation to various phases of management, critical discussion of the ideas presented and of practice.

The author recounts his own difficulty when he first entered this important field, through inability to locate help in the literature. He hopes to have aroused interest in the importance of the broader aspects of the subject, even if he may not always have succeeded in going into sufficient detail on the production side. The need seems to be recognized for separation from mere bookkeeping, to be not merely statistical, in order that cost accounting may be a proper scientific basis for policy building, independent of mere management.

Hempelmann clearly recognizes that in the necessities which arise in manufacturing, the demand for quick, ready information as to cost forces the cost accountant as well as the management into short-cut and make-shift methods which are of practical value for the time being, but which become so intricate that it is next to impossible to follow properly economic principles and detect false steps to the extent that is desirable.

The author thoroughly emphasizes at all times the simple fundamental relationships which determine cost of manufacture. He seems to be at home in the citation of illustrations from a variety of chemical industries. The work, however, has almost no diagrammatic or tabulated illustrations from actual experience and contains some apparent chemical blunders. For instance, on p. 88 "general theory" is stated to credit 1000 kg. of "salpeter" with the recovery of "7000 kg." of 100 per cent HNO_3, whereas practice is credited with ability only to return a yield of 65 per cent against this "70 per cent."

The author calls attention to the fact that those who wish technical information as to how cost accounting should be carried out in particular industries in chemical business will naturally be disappointed in the sketchy character of his discussions. Nevertheless, the reviewer feels that any one interested in the philosophy of this problem will profit by a study of this contribution.

James R. Withrow

Wärmewirtschaftsfragen. Monographien zur Feuerungstechnik, Heft 5. By L. Litinsky. 194 pages. Otto Spamer, Leipzig, 1923. Price, $1.10.

This treatise on fuel economy in industrial works was written with a view of explaining the present practices in the saving of heat, and of adding something for increasing the scope of this important field. The book represents a revised and supplemented collection of a number of the author's own papers which have been published in various technical journals. Since most of these articles are now out of print, the material has been collected and presented in the form of a fairly unified book adapted to meet the needs of the practical fuel or heat engineer. The necessary theory and mathematics are presented in a very elementary manner, and the applications are illustrated by the use of many commercial examples.

The author has not attempted to cover here the entire field of industrial heat economy. In fact, one might say that the treatise concerns itself with problems of glass works, ceramic manufactures, and the devices used in connection with these industries, such as gas producers, regenerators, and furnaces.

The book is divided into eight parts, the first of which involves computations applicable to a gas-heated, kiln-burning refractory ware, and includes dimensions and characteristics of the oven, chimney, gas mains, and the producer-gas generator. Many other things, such as temperatures, efficiencies, fuel consumption, and products of combustion are also treated here.

The second topic, "Heat Balance Sheet of a Glass Smelting Oven," explains how the grate losses of the gas generator, the cooling of the gas in the mains, the radiation, conduction, and convection losses in the oven, and the latent heats of the byproducts, are all balanced against the total calorific value of the fuel consumed and the reaction heats of the materials used in making the glass.

The third part gives very briefly the economic reasons for the manufacture of gas from wood and peat in certain localities. This is followed in the next part by a comparison of regenerators and recuperators, including typical heat balance sheets for each. The fifth section concerns itself with kinds of gas generators, applicability of low-grade fuels, determination of combustion temperatures, gas analyses, and important methods of economizing heat. Part Six, on the determination of the consumption of heat in the distillation of coal, brings in also the various methods of measuring gases, while the two remaining brief parts are on the determination of flue losses by analysis of the outgoing gases, and the comparison of the dry and wet methods of extinguishing coke.

G. R. Greenslade

NEW BOOKS

Advanced Practical Physics for Students. B. L. Worsnop and H. T. Flint. 640 pp. Price, $8.00. E. P. Dutton & Co., New York.

Aluminium Repairing. William H. H. Platt. 77 pp. Illustrated. Price, $1.50. D. Van Nostrand Co., New York.

Annual Reports on the Progress of Chemistry for 1922. Vol. XIX. The Chemical Society (London). 321 pp. Price, $3.00. D. Van Nostrand Co., New York.

Applied Calculus. An Introductory Textbook. F. F. P. Viscare. 460 pp. Illustrated. Price, $3.75. D. Van Nostrand Co., New York.

Applied Optics. The Computation of Optical Systems. Adolph Steinheil and Ernest Voit. Translated and edited by James Weir French. **Vol. I.** 187 pp. **Vol. II.** 205 pp. Price, $5.00 each, $9.00 the set. D. Van Nostrand Co., New York.

Atoms. Jean Perrin. Translated by D. L. Hammick. 246 pp. Illustrated. Price, $2.50. D. Van Nostrand Co., New York.

Boy's Own Book of Science. Floyd L. Darrow. 331 pp. Price, $2.50. The Macmillan Co., New York.

Bureau Bulletin of the British Cast Iron Research Association. No. 1. 102 pp. British Cast Iron Research Association, Birmingham.

By-Product Coking. G. Stanley Cooper. 2nd edition. 192 pp. Price, $4.50. D. Van Nostrand Co., New York.

Civilization and the Microbe. Arthur I. Kendall. Price, $2.50. Houghton Mifflin Co., Boston.

Cotton Industry. J. H. Crabtree. 126 pp. Price, $2.00. D. Van Nostrand Co., New York.

Discovery, or The Spirit and Service of Science. Richard Gregory. American edition. 347 pp. Illustrated. Price, $2.00. The Macmillan Co., New York.

Elementary Steam Power Engineering. Edgar MacNaughton. 590 pp. Illustrated Price, $5.00. John Wiley & Sons, Inc., New York.

Everyday Mysteries. Secrets of Science in the Home. Charles Greeley Abbot. Young People's Shelf of Science. 198 pp. Price, $2.00. The Macmillan Co., New York.

Fabrication du Vinaigre, d'après les Procédés les plus recents. J. Fritsch. 339 pp. Illustrated. Price, $3.00. D. Van Nostrand Co., New York.

Forge, Chaudronnerie, Ajustage. M. Houa. 132 pp. Price, 6 fr. Illustrated. Dunod, Paris.

General Chemistry. Horace G. Deming. 605 pp. Price, $3.50. John Wiley & Sons, Inc., New York.

Laboratory Directions in Inorganic Chemistry. Alexander Silverman. 2nd edition, revised. Illustrated. Price, $1.25. D. Van Nostrand Co., New York.

Laboratory Experiments in Practical Physics to Accompany the Revised Edition of Black and Davis' "Practical Physics." N. Henry Black. 241 pp. Price, $1.00. The Macmillan Co., New York.

Laboratory Manual of Inorganic Chemistry. John B. Ekeley. 2nd edition, revised. 225 pp. Price, $1.50. John Wiley & Sons, Inc., New York.

Manufacture of Lubricants, Shoe Polishes, and Leather Dressings. Richard Brunner. Translated from the 6th German edition. 3rd edition, revised and enlarged. 252 pp. Price, $4.00. D. Van Nostrand Co., New York.

Mechanical Engineers' Handbook. Robert T. Kent, Editor-in-Chief. 10th edition, rewritten and enlarged. 2247 pp. Illustrated. Price, $7.00. John Wiley & Sons, Inc., New York.

Modern Chemistry, Pure and Applied. Vol. VI. Arthur J. Hale. 287 pp. Illustrated. Price, $4.00. D. Van Nostrand Co., New York.

Modern Gas Producers. N. E. Rambush. 545 pp. Price, $15.00. D. Van Nostrand Co., New York.

Oil and Gas Engine Power. Albert W. Daw and Zacharias W. Daw. 468 pp. Illustrated. Price, 45 s. net. Constable & Co., London.

Outline for Qualitative Analysis. Herbert O. Smith. 4 pp. Price, $0.10. D. Van Nostrand Co., New York.

Outlook for Research and Invention. Nevil Monroe Hopkins. 256 pp. Price, $2.00. D. Van Nostrand Co., New York.

Petroleum Resources of the World. Valentin R. Garfias. 243 pp. Illustrated. Price, $3.00. John Wiley & Sons, Inc., New York.

Practical Optics. B. K. Johnson. 189 pp. Price, $3.75. D. Van Nostrand Co., New York.

Practical Polishing and Staining. A. W. Parkhouse. 128 pp. Price, $3.00. D. Van Nostrand Co., New York.

Structural Design in Theory and Practice. Henry Adams. 2nd edition. 265 pp. Price, $3.50. D. Van Nostrand Co., New York.

Systematic Inorganic Chemistry. From the Standpoint of the Periodic Law. R. M. Caven and G. D. Lander. New edition. 478 pp. Price, $3.00. D. Van Nostrand Co., New York.

Textbook of Intermediate Physics. H. Moore. 824 pp. Price, $9.00. E P. Dutton & Co., New York.

Treatment of Paper for Special Purposes. Louis Edgar Andés. Translated from the German. 2nd English edition, revised and enlarged 216 pp. Price, $3.50. D. Van Nostrand Co., New York.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Notice—*Any publications mentioned under this heading will be sent free, unless otherwise noted, to readers of This Journal, on request to the firm issuing the publication. When writing for any of these items kindly mention Industrial and Engineering Chemistry.*

Abbé Specialties. Catalogs A, B, C, E, G, H, covering crushing, cutting, grinding, mixing, pulverizing, and sifting machinery. 8 to 32 pp. Paul O. Abbé, Inc., 73 Murray St., New York, N. Y.

Acimet Valve. Catalog showing patterns, sizes, and prices of corrosion-resistant valves. 24 pp. Cleveland Brass Mfg. Co., 4606 Hamilton Ave., N. E., Cleveland, Ohio.

Barnstead Water Stills. General catalog showing uses and applications of this apparatus, with specifications and tables. 34 pp. Barnstead Still & Sterilizer Co., Inc., Boston, Mass.

Beach-Russ Rotary Pumps. *Bulletin* **32,** illustrating and describing this equipment. 8 pp. Beach-Russ Co., 50 Church St., New York, N. Y.

Brown Electrical Indicating and Recording CO_2 Meters. *Catalog* **30.** Contains diagrams, illustrations, and instructions concerning application and use of these meters. 8 pp. Brown Instrument Co., Philadelphia, Pa.

Buflovak Apparatus for Producing Dry and Evaporated Milk Products. New booklet showing applications of this equipment, with useful data and tables. 36 pp. Buffalo Foundry & Machine Co., 1549 Fillmore Ave., Buffalo, N. Y.

California Redwood. Brochure giving interesting and instructive information in regard to general and industrial uses of this material. 36 pp. Pacific Lumber Co., McCormick Bldg., Chicago, Ill.

Chemical and Metallurgical Laboratory Supplies. *General Catalog* **AA,** showing complete line of such equipment and supplies with illustrations, specifications, and prices. Cloth. 606 pp. Eimer & Amend, Third Ave., 18th to 19th Sts., New York, N. Y.

Chemical Equipment of Metal. Catalog illustrating and describing Bethlehem apparatus. 48 pp. Bethlehem Foundry & Machine Corp., Room 1716, Grand Central Terminal, New York, N. Y.

Chemicals and Drugs. 206 pp. Eimer & Amend, New York, N. Y.

Christie Dryers, Calciners, Coolers. Illustrated treatise covering the design and application of such equipment for the chemical industries, with data and charts of special interest to the chemical engineer. 16 pp. L. R. Christie Co., 307 Fourth Ave., Pittsburgh, Pa.

CO_2 Recorder Accessories. *Bulletin* **116-A,** describing three new accessories in this line designed to reduce operating attention. 8 pp. Uehling Instrument Co., 473 Getty Ave., Paterson, N. J.

Current Duriron Literature. Bulletin revised to September, 1923, giving complete data and tables on uses and applications of Duriron corrosion-resistant metal. 48 pp. Loose-leaf with binder. Duriron Co., Dayton, Ohio.

Data concerning Platinum. General catalog covering the subject, with tables and sizes, capacities, and weights. 88 pp. Baker & Co., Inc., Murray and Austin Sts., Newark, N. J.

Dopp Equipment. *Catalog* **VII,** describing seamless-jacketed kettles, mixers, vacuum and pressure apparatus. 64 pp. Sowers Manufacturing Co., Buffalo, N. Y.

Duriron Acid-Proof Drain Pipe. 24 pp. Duriron Co., Dayton, Ohio.

Electric Furnaces for the Laboratory. 22 pp. Norton Co., Worcester, Mass.

Electrical Instruments for Ion Concentration Measurements. Brown Instrument Co., Philadelphia, Pa.

Elementary Photographic Chemistry. A technical treatise on this subject, containing much valuable information and precise data of interest to those engaged in this special field. 80 pp. Eastman Kodak Co., Rochester, N. Y.

Elyria Glass Enameled Equipment. *Bulletin* **31.** Technical treatise on glass-enameled ware for the chemical, pharmaceutical, and allied industries. 20 pp. The Elyria Enameled Products Co., Elyria, Ohio.

Engelhard Equipment. Series of bulletins in loose-leaf binder, covering impervite porcelain and refractories, LeChatelier pyrometers, electric thermometers, electric furnaces, and quartz glass. Charles Engelhard, Inc., 30 Church St., New York, N. Y.

Hard Rubber Chemical Equipment. Bulletins on hard rubber pumps, pipe, fittings and utensils. Loose-leaf with binder. American Hard Rubber Co., 11 Mercer St., New York, N. Y.

Hartman Sterilizers. A series of bulletins in loose-leaf binder, describing, with illustrations and charts, this electrolytic water-purifying apparatus. 24 pp. United States Ozone Co., Scottdale, Pa.

Heusser Precision Balances. *Bulletin* **65,** containing tables of dimensions and weights, with illustrations. 24 pp. The Mine & Smelter Supply Co., P. O. Box 119, Denver, Colo.

Kewaunee Book of Laboratory Furniture. New edition. General catalog covering complete line of this manufacturer. Cloth. 408 pp. Kewaunee Mfg. Co., Kewaunee, Wis.

Knight Chemical Stoneware. General catalog fully describing and illustrating this apparatus, with comprehensive data and illustrations. 54 pp. Maurice A. Knight, Kelly Ave., East Akron, Ohio.

Koerting Condensers and Recooling Systems. Group of bulletins in loose-leaf binder covering multi-jet condensers, atmospheric heating valves, high-vacuum, air-jet oil pumps, recooling nozzles, vacuum traps, oil separators, etc. 60 pp. Schutte & Koerting Co., 12th and Thompson Sts., Philadelphia, Pa.

Material of a Thousand Uses. Brochure, illustrated in color, describing the uses and applications of the phenol condensation products, Bakelite, Condensite, and Redmanol. 24 pp. Bakelite Corp., 8 West 40th St., New York, N. Y.

Norton Refractories, Alundum-Crystolon. Fused alumina refractories and laboratory ware. Catalog. 64 pp. Norton Co., Worcester, Mass.

Physical Apparatus and General Laboratory Supplies. *Catalog* **H-D.** 1923. 106 pp. Wm. Gaertner & Co., 5345 Lake Park Ave., Chicago, Ill.

Potentiometer Pyrometers. *Catalog* **87,** containing comprehensive and valuable data and charts in regard to pyrometer practice. 44 pp. Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia, Pa.

Proctor Dryers for Cotton. Illustrated handbook covering application of drying equipment for cotton. Fully illustrated. 32 pp. Proctor & Schwartz, Inc., Philadelphia, Pa. (Also published by same firm: **Proctor Dryers for Hair, Leather, Silk Piece Goods, Knit Goods and Cloth; Proctor Dryers for Yarn.**)

Pulverizing, Grinding, and Mixing Machinery. *Bulletin* **20,** giving technical data on this subject, with tabular matter and illustrations. 12 pp. Abbé Engineering Co., 50 Church St., New York, N. Y.

"Scientia" and "Studentia" Calorimeters. *Catalog* **C.** 34 pp. Wm. Gaertner & Co., 5345 Lake Park Ave., Chicago, Ill.

Sharples Super Centrifuges. Illustrated bulletin on commercial applications of this type of equipment. Diagrams and complete exposition, list of processes successfully employing the super-centrifugal systems. 24 pp. The Sharples Specialty Co., 23rd and Westmoreland Sts., Philadelphia, Pa.

Sperry Filter Press. *Catalog* **14,** containing illustrations, charts, and technical data on the use and application of filter press equipment of special interest to the chemical engineer. 60 pp. D. R. Sperry & Co., Batavia, Ill.

Standard Laboratory Apparatus. Adopted by the Manufacturing Chemists Association of the United States. 50 pp. Eimer & Amend, New York, N. Y.

Stokes Pharmaceutical and Chemical Apparatus. General catalog with complete data and illustrations. 100 pp. F. J. Stokes Machine Co., Cedar Grove Station, Philadelphia, Pa.

Swenson Evaporators. *Technical Bulletin* **E-122.** Illustrated. 16 pp. Swenson Evaporator Co., Harvey, Ill.

The Truth about Ozone. 64 pp. United States Ozone Co., Scottdale, Pa.

Vertical Cylindrical Electric Furnaces. *Instruction Book* **88,712.** Loose-leaf bulletin with illustrations, diagrams, and much technical data on electric furnaces for various uses. 26 pp. General Electric Co., Schenectady, N. Y.

Vitreosil Data. Technical booklet giving useful data, tables, and prices on fused silica ware. 16 pp. Thermal Syndicate, Ltd., 350 Madison Ave., New York, N. Y.

Spring Meeting Reservations

Members planning to attend the spring meeting of the Society, which will be held in Washington, D. C., during the week of April 21, 1924, should make their reservations now. The meeting will be held at the time when the hotels will be overcrowded, and in order to be sure of good accommodations reservations should be made immediately. The New Willard has been chosen as hotel headquarters, but if you do not desire to write to the hotel directly requests for reservations may be sent to H. C. Fuller, chairman of the Committee on Hotels and Transportation, Institute of Industrial Research, 1845 B Street, N. W., Washington, D. C.

GOVERNMENT PUBLICATIONS

Commerce Reports—September

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

A national **gas exhibition** was held at Bingley Hall, Birmingham, England, from September 17 to October 3, 1923, for the purpose of demonstrating and further popularizing the service and use of gas in home and industry. (P. 612)

Producers of china clay are much interested in experiments that are being conducted on the use of **fuel oil** in drying their product in Cornwall and Devon. A six months' test has demonstrated a considerable saving over coal and that fuel-oil plants are adapted to existing kilns and furnaces. (P. 621)

Recent regulations of the Polish government provide that producers of **crude oil** must declare to the State oil bureau on or before the 15th of each month their gross production for the preceding month. The State oil bureau, in turn, shall signify before the 10th of the month whether they will purchase the oil produced during the preceding month. If the State oil bureau does not indicate a desire for the oil then it is available for the general market. (P. 621)

There is a fair market for **disinfectants** in Hongkong and a growing demand for sanitary disinfectants in the Canton consular district. (Pp. 629–30)

The coefficient of increase of 2.5, by which the basic import duties on **crude iodine** have been multiplied since December 2, 1922, has been removed by a French law. (P. 638)

New processes have resulted in the extraction of **crude rubber** in North Central Mexico containing less than one-half of 1 per cent of water, and it is possible that there may be a revival of the industry which formerly brought considerable wealth to this district. (P. 650)

The Mexican government has under consideration a project for the encouragement of the use of oil for **household fuel** and cooking purposes as a part of its campaign to conserve the forest resources of Mexico. (P. 671)

The growth of the Peruvian **fuel oil** trade during the past three years is quite notable. An important development is the recent substitution of the native oil in place of coke in the largest smelter of the republic. (P. 672)

The new substitute for gasoline, called **"Dynalkol"** was recently tested in a number of flights made by the Czechoslovak Aviation Service, and has proved to be even more efficient than gasoline. The Czechoslovak government is planning exhaustive tests with this new fuel. (P. 672)

The foreign trade of the United States in **chemicals** and **allied products** for the month of July, 1923, as compared with the corresponding month of last year, showed an expansion of 48 per cent in exports. (P. 676)

The German **chemical industry** in the first half of 1923 is reviewed. (Pp. 677–8)

During 1922 the **asbestos** sold and shipped from the mines of Quebec amounted to 160,339 tons, as compared with 87,475 tons in 1921. (Pp. 680–1)

Recent press items report the appointment of a Canadian commission consisting of five members, to inquire into the forest resources of Canada and to determine the necessity for placing an embargo upon the exportation of **pulpwood** from Canada. (P. 717)

It is expected that a bill will be introduced in the Australian parliament abolishing the import duty on **sulfur** and granting a bounty to domestic producers of sulfur. (P. 718)

Certain changes in **patent**, design, and trade-mark **law** of Germany are cited. (P. 719)

A royal decree of Greece extends the time during which the requirements of the **patent law** with respect to working the invention and paying the fees may be complied with and forfeiture of the patent avoided. (P. 719)

The situation in **heavy chemicals** in France in August was calm, with little change in prices. **Secondary chemicals** were relatively active, **tannery stocks** were small, the **dye situation** was calm, and there was slack demand for **paint-making materials.** (P. 724)

At a recent conference of the Sugar Club in Havana it was decided that hereafter the **standard temperature** for graduation of Brix hydrometers for the laboratories exchanging information under the club agreement shall be 17.5° C. (P. 731)

According to a review of the Mexican **paint situation,** Mexico presents a good field for the sale of American paints, and it is pointed out that unsuccessful bids may lead to future business. (Pp. 732–3)

Netherlands India, which admits **chemical fertilizers** free of duty, offers a good field for the American product. (Pp. 733–4)

The French occupation of the Ruhr Valley has had no apparent effect on the **chemical** and **dye trade** of Germany in Mexico. The prices of German dyes and chemicals in Mexico have not increased and representatives of American manufacturers of dyes and chemicals report that they can note no increase in orders since the occupation of the Ruhr. (P. 734)

There is a good demand for **paints** in Mexico City. White lead and paste ground in oil meet an especially ready sale, although throughout most of Mexico water paints are in greater demand. (Pp. 735–6)

A portion of the coast of Lower California is the source of a small quantity of seaweed, which is processed for the production of **vegetable gelatin** or **agar-agar.** (P. 736)

The original French text and a translation or summary in English of the various French decrees relating to the compulsory purchase of **industrial alcohol** by importers of gasoline is on file in the Petroleum Division of the Bureau of Foreign and Domestic Commerce and may be consulted by interested parties. (P. 741)

Greek **import duties** have been modified on paraffin wax, ceresin, and all mineral wax not specified; on naphthalene, monosulfide, sulfate, hyposulfide, hypochloride of soda, chloride of lime, and chloride of magnesium; and on celluloid, gluten, casein, imitation amber, and similar materials. (P. 765)

Changes have been made in the Argentine export duty on **linseed.** (P. 766)

The duty on heavy oils, residues of petroleum, and other **mineral oils** imported into St. Pierre and Miquelon, France, has been reduced from 6 francs to 0.10 franc per 100 kilos. (P. 767)

The Chilean **nitrate industry** has succeeded in working itself out of a very critical position and is once more on a stable basis. The great prosperity in the metal trades in the United States has also resulted in a greatly increased demand for Chilean **copper,** Chile's second important export staple. (P. 778)

The **crude rubber survey** authorized by Congress and undertaken by the Department of Commerce is now under way in every region where investigations were originally planned. After the return of the parties composing the various expeditions to Washington their separate findings will be assembled in the form of a complete report. (Pp. 800–1)

The effect of monopoly on the **camphor industry** and trade is described, and it is pointed out that the restrictions of the Japanese monopoly have resulted in various countries encouraging the domestic production of natural camphor and have also stimulated efforts to solve the problem of the profitable manufacture of synthetic camphor. (Pp. 808–11)

The production of **crude mineral oil** in France decreased 50 per cent for the second quarter of 1923. (P. 819)

A decree by the Polish Ministers of Finance and Industry and Commerce provides for a reduction of certain duty coefficients on **fertilizers,** certain **chemical products,** and **oils** for the manufacture of margarine and other edible fats. (P. 833)

The production in Soviet Russia of all the **basic chemicals,** as well as **fertilizer,** showed a steady increase during the first half of 1923. Production statistics are given for these chemicals divided into three groups—acids, alkalies, and salts. (P. 841)

STATISTICS OF EXPORTS TO THE UNITED STATES

- Curacao—(P. 620)
  - Crude oil
- Shanghai—(P. 649)
  - Antimony
  - Camphor, crude
  - Wood oil, Chinese
- Constantinople—(P. 711)
  - Licorice root
  - Manganese ore
  - Opium
- Hongkong—(P. 735)
  - Anise oil
- **Japan—(Pp. 734 and 771)**
  - **Agar agar**
  - **Camphor**
- **Canada—(P. 742)**
  - **Pulpwood**
- **Austria—(P. 744)**
  - Magnesite
- **Africa—(P. 781)**
  - **Blister copper**
  - **Chrome ore**

SPECIAL SUPPLEMENTS ISSUED

Petroleum in Foreign Trade and Services of the Petroleum Division.

The German Coal-Tar Chemical Industry: Production, Export, and Import Statistics. *Trade Information Bulletin* **141.**

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Mines

Anthracite Substitutes. O. P. Hood. *Reports of Investigations* 2519. 4 pp. Issued August, 1923.

Comparative Engine Tests with Crude, Acid-Refined, and Silica-Gel Refined Motor-Benzol. A. C. Fieldner and G. W. Jones. *Reports of Investigations* **2517.** 3 pp. Issued August, 1923.

Effect of Cooling Systems on Evaporation Losses of Gasoline. Ludwig Schmidt. *Reports of Investigations* **2531.** 12 pp. Issued September, 1923.

Eighth Semiannual Motor Gasoline Survey. N. F. LeJeune and H. M. Smith. *Reports of Investigations* **2525.** 3 pp. Issued September, 1923.

Forms of Sulfur in Steamed Coke and Their Action in the Blast Furnace. J. H. Thompson. *Reports of Investigations* 2518. 7 pp. Issued August, 1923.

Fuels Available for Domestic Use as Substitutes for Anthracite Coal. Rudûlf Kudlich. *Reports of Investigations* **2520.** 7 pp. Issued August, 1923.

Leaching Nonsulfide Copper Ores with Sulfur Dioxide. C. E. Van Barneveld and E. S. Leaver. *Technical Paper* **312.** 91 pp. Paper, 20 cents.

Oxygen-Oil Explosions. Preliminary Report II. Spontaneous Ignition of Metals in Oxygen under Pressure. J. J. Jakowsky and E. W. Butzler. *Reports of Investigations* **2521.** 4 pp. Issued September, 1923.

Preparation and Detonating Properties of Cyanuric Triazide. C. A. Taylor and W. H. Rinkenbach. *Reports of Investigations* 2513. 4 pp. Issued August, 1923.

Progress in Blast-Furnace Research. P. H. Royster, T. L. Joseph, and S. P. Kinney. *Reports of Investigations* 2524. 6 pp. Issued September, 1923.

Strength and Sensitiveness of TNT as Determined by the Laboratory "Sand-Test" Bomb. C. A. Taylor and R. D. Leitch. *Reports of Investigations* **2526.** 5 pp. Issued September, 1923.

Survey of Pacific Coast Petroleum Products. Part III. Burning and Fuel Oils. E. C. Lane and N. F. LeJeune. *Reports of Investigations* **2511.** 11 pp. Issued August, 1923.

Tests of a Powdered-Coal Plant. A Report of Investigations at the Power Plant of the St. Joseph Lead Co., Rivermines, Mo. Henry Kreisinger, John Blizard, C. E. Augustine, and B. J. Cross. *Technical Paper* **316.** 22 pp. Paper, 5 cents.

The Electrothermic Metallurgy of Zinc. B. M. O'Hara. *Bulletin* **208.** 106 pp. Paper, 15 cents. This bulletin represents work done under a cooperative agreement between the Bureau of Mines, Department of the Interior, and the Missouri School of Mines and Metallurgy.

The Use of Highly Volatile Natural-Gas Gasoline as a Refrigerant. L. D. Wyant. *Reports of Investigations* **2510.** 10 pp. Issued August, 1923.

Water-Gas Tar Emulsions. W. W. Odell. *Technical Paper* **304.** 51 pp. Paper, 10 cents. This paper represents work done under a coöperative agreement between the Bureau of Mines, Department of the Interior, the State Geological Survey Division of the State of Illinois, and the Engineering Experiment Station of the University of Illinois.

Bureau of Fisheries

Northwestern Lakes of the United States: Biological and Chemical Studies with Reference to Possibilities in Production of Fish. George Kemmerer, J. F. Bovard, and W. R. Boorman. *Document* **944.** 92 pp. Paper, 25 cents.

Bureau of Foreign and Domestic Commerce

A World Resumé of the Paint Situation with Statistical Tables Showing Complete Exports from the United States for 1922. *Special Circular* **9,** Chemical Division. 24 pp.

Bureau of the Census

Essential Oils. Census of Manufactures, 1921. 8 pp. Paper, 5 cents.

Explosives. Census of Manufactures, 1921. 10 pp. Paper, 5 cents.

Paper and Wood Pulp. Census of Manufactures, 1921. 17 pp. Paper, 5 cents.

Salt. Census of Manufactures, 1921. 7 pp. Paper, 5 cents.

Department of Agriculture

An Improved Method for the Determination of Nicotine in Tobacco and Tobacco Extracts. O. M. Shedd. *Journal of Agricultural Research,* **24** (June 16, 1923), 961–70.

A Study of Factors Affecting the Nitrogen Content of Wheat and of the Changes That Occur during the Development of Wheat. G. A. Olson. *Journal of Agricultural Research,* **24** (June 16, 1923), 939–53.

Apple By-Products as Stock Foods. G. P. Walton and G. L. Bidwell. *Department Bulletin* **1166.** 40 pp. Issued July 26, 1923. Paper, 5 cents.

Effect of Different Concentrations of Manganese Sulfate on the Growth of Plants in Acid and Neutral Soils and the Necessity of Manganese as a Plant Nutrient. J. S. McHargue. *Journal of Agricultural Research,* **24,** (June 2, 1923), 781–94.

Efficiences of Phosphatic Fertilizers as Affected by Liming and by the Length of Time the Phosphates Remained in Porto Rican Soils. P. L. Gile and J. O. Carrero. *Journal of Agricultural Research,* **25** (July 28, 1923), 171–95.

Growth-Promoting Value of the Proteins of the Palm Kernel, and the Vitamin Content of Palm-Kernel Meal. A. J. Finks and D. B. Jones. *Journal of Agricultural Research,* **25** (July 28, 1923), 165–9.

Nutritive Value of Mixtures of Proteins from Corn and Various Concentrates. D. B. Jones, A. J. Finks, and C. O. Johns. *Journal of Agricultural Research,* **24** (June 16, 1923), 971–8.

Geological Survey

Arsenic in 1922. V. C. Heikes and G. F. Loughlin. Separate from Mineral Resources of the United States, 1922, Part I. 24 pp. Published September 17, 1923.

Clay in 1922. Jefferson Middleton. Separate from Mineral Resources of the United States, 1922, Part II. 8 pp. Published October 10, 1923.

Fuller's Earth in 1922. Jefferson Middleton. Separate from Mineral Resources of the United States, 1922, Part II. 3 pp. Published September 15, 1923.

Magnesium and Its Compounds in 1922. J. M. Hill and G. F. Loughlin. Separate from Mineral Resources of the United States, 1922, Part II. 17 pp. Published September 20, 1923.

Mineral Resources of the United States, 1921. Part I—Metals. G. F. Loughlin. 766 pp. Price, $1.00. A consolidation of reports on the different metals published separately between May, 1921, and July, 1922, with a summary covering both metals and nonmetals

Quicksilver in 1922. F. L. Ransome. **With a Supplementary Bibliography.** I. P. Evans. Separate from Mineral Resources of the United States, 1922, Part I. 12 pp. Published September 18, 1923.

Strontium in 1922. G. W. Stose. Separate from Mineral Resources of the United States, 1922, Part II. 3 pp. Published September 12, 1923

Surface Water Supply of Hawaii July 1, 1918, to June 30, 1919. N. C. Grover, C. T. Bailey, and J. E. Stewart. *Water-Supply Paper* **515.** 123 pp. Paper, 15 cents. Prepared in coöperation with the Territory of Hawaii.

Surface Water Supply of the United States 1919-1920. Part VI—Missouri River Basin. N. C. Grover, W. A. Lamb, Robert Follansbee, W. G. Hoyt, and R. C. Rice. *Water-Supply Paper* **506.** Prepared in coöperation with the States of Montana, Wyoming, Iowa, Colorado, and Kansas. 411 pp. Paper, 35 cents.

The Twenty-Mile Park District of the Yampa Coal Field, Routt County, Colorado. M. R. Campbell. *Bulletin* **748.** 82 pp. Paper, 20 cents.

Tin in 1922. B. L. Johnson. Separate from Mineral Resources of the United States, 1922, Part I. 4 pp. Published October 11, 1923.

Public Health Service

Collection and Preservation of Blood Samples for Determination of Carbon Monoxide. R. R. Sayers, H. R. O'Brien, G. W. Jones, and W. P. Yant. *Public Health Reports,* **38** (August 31, 1923), 2005–11.

On the Composition of the Precipitate from Partially Alkalinized Alum Solutions. L. B. Miller. *Public Health Reports,* **38** (August 31, 1923), 1995–2004.

Public Health Service Publications. A List of Publications Issued between October, 1922, and April, 1923. *Reprint* **338** from *Public Health Reports.* 4 pp.

Sewage Treatment in the United States. Report on the Study of Fifteen Representative Sewage Treatment Plants. H. H. Wagenhals and Others. *Public Health Bulletin* **132.** Price, 50 cents.

State Laws and Regulations Pertaining to Public Health, 1920. Jason Waterman and Others. *Supplement* **43** to *Public Health Reports.* Paper, 25 cents.

The Elimination of Carbon Monoxide from Blood, by Treatment with Air, with Oxygen, and with a Mixture of Carbon Dioxide and Oxygen. R. R. Sayers and W. P. Yant. *Public Health Reports* **38** (September 7, 1923), 2053–74.

Tariff Commission

Census of Dyes and Other Synthetic Organic Chemicals, 1922. *Tariff Information Series* **31.** 185 pp. Paper, 20 cents.

MARKET REPORT—OCTOBER, 1923

[SUPPLIED BY DRUG & CHEMICAL MARKETS]

WHILE the volume of business during the month has been showing a steady increase over that of the preceding month, the total volume has not been up to expectations of leading interests in industrial chemicals. Demand has been spotty for the greater part of the period, but with the approach of the season for making contracts for the coming year buying is expected to become steadier. Consuming industries have been slow in recovering from the usual summer depression. Textile mills, especially in New England, have been showing little increased activity and several mills have announced curtailment of operations from half-time to closing for indefinite periods. Continued warm weather for the season of the year has also had its effect upon buying in general.

Although there has been no general announcement in alkali prices, it is understood that other manufacturers will maintain their former selling prices for contracts for the coming year similar to those recently announced by one manufacturer. Demand for alkalies has been increasing steadily but prices have shown no change or fluctuation in over two years. Cost of production has increased, but the increased consumption has offset to some extent the difference in operation advances. Bleaching powder has been subject to much price-cutting during the summer and early fall. Keen competition and a slackening demand has caused sellers to disregard formal and open prices for their own private terms wherever business has been available. Sales have been reported as low as $1^1/_8$ cents per pound at the works.

On the first of the month a reduction in the price of bleach for the last quarter from $1.75 to $1.65 was announced by a leading maker. Continued weakness in the market, however, forced another reduction on the 15th to $1.25 for October delivery, and $1.50 for November and December. Contract prices for the coming year were also announced for chlorine and bleaching powder. Contract prices for next year have been announced by a leading maker of bichromates and they are the same as those which ruled during 1923. One maker of bichromates has reduced sodium bichromate to $7^1/_8$ cents a pound for car-lot quantities, which is considerably under the announced contract prices. Competition for bichromate business has been very keen. Heavy acids have been moving fairly well, with sulfuric acid in greatest demand. Formic acid has been active and supplies are stated to be small in the face of present demand. Lactic acid continues in steady demand.

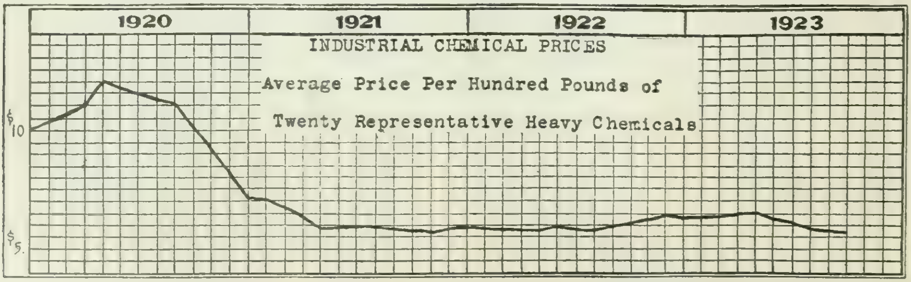
Arsenic has been receiving more attention recently and prices have advanced owing to more active demand and a scarcity of supplies in the market. Japan has not been offering arsenic during the past month and German import prices are above domestic and local prices. Domestic producers are understood to have little to offer. Recent lack of demand for copper and slowing up of smelters may have some effect upon the domestic output of arsenic, since it is a by-product of the copper smelters. The season for calcium arsenate is over and makers are beginning to prepare for next season. Ammonium chloride is stronger and higher in price. Barium products have been strong, especially the carbonate, domestic makers being well sold ahead and imported material difficult to obtain. Barium chloride is firm and shipments from abroad are higher. Acetone continues in limited supply. Copper sulfate has been declining slightly with the drop in metallic copper prices.

Domestic caustic potash has been reduced to the level quoted by importers of German potash. Potassium chlorate is firm at recent levels. Prussiates have shown no improvement in demand and prices are lower for both sodium and potassium prussiates. Demand for colors made from prussiates has been lacking, and sellers have been forced to reduce prices in order to move their stocks. Imported potassium permanganate is higher at $17^3/_4$ cents per pound while domestic material is unchanged at 17 cents at works. Soda ash and caustic soda continue in steady demand. Export demand for caustic soda has shown a slight improvement. Sodium sulfide is beginning to improve after a dull summer. Glauber's salt is in slightly better demand at unchanged prices. Formaldehyde is easier on accumulation of stocks and small demand.

Crude coal-tar products have been showing steady decline in prices. Benzene and toluene are lower owing to an accumulation of stocks and the lower market in gasoline in competition with which 90 per cent benzene is sold. Demand has been spotty and buyers are not inclined to anticipate their requirements for the future. Solvent naphtha and xylene are slightly lower. Phenol had been holding fairly steady until about the middle of the month when one seller announced a reduction to 26 cents a pound, a decline of 2 cents a pound below previous levels. Cresylic acid has been fairly active with prices at former levels. Pyridine is very scarce and prices have advanced to $6.00 and above for material on spot. Shipments are difficult to obtain from abroad and domestic production is insufficient for present needs.

Intermediates have been moving slowly owing to the poor demand for colors. The situation is controlled by manufacturers, however, and little is being produced except as required for routine consumption. Prices have remained steady during the dull period, except for occasional lots in the resale market. With increased demand prices will probably become firmer, but no sharp advances are expected. Salicylates have been steady in price and demand with the statistical position firm. Medicinal chemicals have been moving in a seasonal way.

Vegetable, animal, and fish oils have been more active and prices have shown an upward trend. Linseed oil is higher, though the demand is mainly routine in character.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

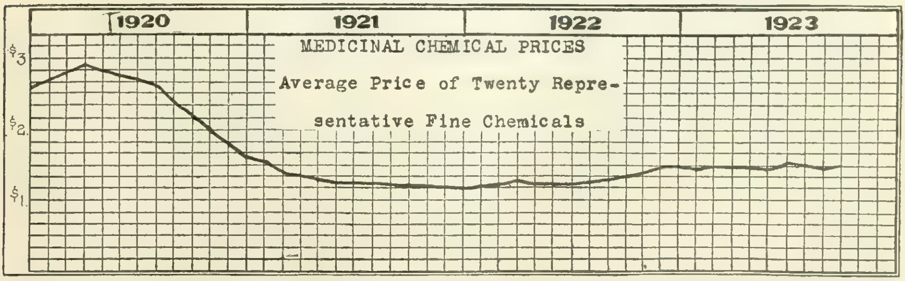
INORGANIC CHEMICALS

	Oct. 1	Oct. 15	Jan. 1923
Acid, Boric, cryst. bbls.......lb.	.11	.11	.11½
Hydrochloric,comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb.	.73	.73	.65
Nitric, 42°, cbys. c/1 wks.lb.	.06½	.06½	.06
Phosphoric, 50% tech....lb.	.08	.08	.08
Sulfuric, C. P...........lb.	.09	.09	.07
66° tks. wks.......ton	15.00	15.00	15.00
Oleum, 20%.......ton	19.00	19.00	18.00
Alum, Ammonia. lump.......lb.	.03½	.03½	.03½
Potash, lump...........lb.	*.03¼	*.03¼	*.03½
Chrome...........lb.	.05½	.05½	.05½
Soda, ground...........lb.	.04	.04	.04
Aluminum Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd..lb.	.09	.09	.09½
Chloride, white gran.....lb.	.07½	.07½	.07½
Ammonia, anhydrous........lb.	.30	.30	.30
Ammonia Water, drums, 26°.lb.	.07½	.07½	.07½
Arsenic, white..............lb.	.12	.12½	.15½
Barium Choride............ton	*82.50	*82.50	*92.50
Nitrate.................lb.	*.07½	*.07½	*.07½
Barytes, white.............ton	33.50	33.50	33.50
Bleaching Powd., 35%, works .... 100 lbs.	1.65	1.25	2.15
Borax, cryst., bbls...........lb.	.05¾	.05¾	.05½
Bromine, pure, wks..........lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b. N. Y..................ton	24.50	24.50	24.50
Chlorine, liquid.............lb.	.05½	.05½	.05¼
Copper Sulfate......... 100 lbs.	5.00	5.00	6.25
Iodine, resublimed...........lb.	4.55	4.55	4.50
Lead Acetate, white crystals..lb.	.14	.14	.13
Nitrate................lb.	.22	.22	.22
Red.............. 100 lbs.	11.40	11.40	10.60
White (Carb.)..........lb.	.09¾	.09¾	.08½
Lime, live and hydrated, bbl..lb.	.01½	.01½	.01½
Oyster shell............lb.	.03½	.03½	.03
Lime Acetate.......... 100 lbs.	4.00	4.00	3.50
Magnesium Carbonate, tech..lb.	.08	.08	.08
Magnesite, calcined.........ton	55.00	55.00	55.00
Phosphorus, yellow..........lb.	.35	.35	.32
Red...................lb.	.75	.75	*.30
Plaster of Paris, tech ....bbl.	3.30	3.30	3.30
Potassium Bichromate.......lb.	.09½	.09½	.10
Bromide, imported......lb.	.17	*.17	.14½
Carbonate, calc.,80–85%.lb.	*.06½	*.06½	*.05½
Chlorate, cryst.........lb.	*.07½	*.07½	*.05½
Hydroxide, 88–92%.....lb.	*.07¼	*.07	*.08
Iodide, bulk, U. S. P.....lb.	3.75	3.75	3.60
Nitrate................lb.	.06½	.06½	.06½
Permanganate, U. S. P...lb.	*.17½	*.17¾	*.16
Prussiate, red..........lb.	*.60	*.60	*.90
Yellow.............lb.	*.30	*.29	*.38
Salt Cake, bulk............ton	24.00	24.00	28.00
Silver Nitrate...............oz.	.44	.44	.44
Soda Ash, 58%, bags....100 lbs.	*2.00	*2.00	*2.00
Caustic, 76%, N. Y. 100 lbs.	3.70	3.70	3.50
Sodium Acetate.............lb.	.05	.05	.07¼
Bicarbonate....... 100 lbs.	2.25	2.25	2.00
Bichromate............lb.	.07½	.07¼	.07¾
Bisulfite, powd..........lb.	.04½	.04½	.04
Chlorate...............lb.	.06½	.06½	.06½
Cyanide, 96–98%.......lb.	.23	.23	.23
Fluoride, tech...........lb.	.09	.09	.09½
Hyposulfite, bbls... 100 lbs.	2.90	2.90	3.60
Nitrate, 95%...... 100 lbs.	2.45	2.45	2.57½
Nitrite.................lb.	.07¼	.07¼	.08½
Prussiate, yellow........lb.	.14	.14	.18½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40° ....100 lbs.	.80	.80	.80
Sulfide, 60%, fused......lb.	.04½	.04½	.05
Strontium Nitrate...........lb.	*.10	*.10	*.08¾
Sulfur, flowers.........100 lbs.	3.00	3.00	3.00
Crude, mines......long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n....lb.	.12½	.12½	.10¼
Oxide..................lb.	.47	.47	.43
Zinc Chloride, U. S. P........lb.	.25	.25	.20
Oxide, bbls.............lb.	.08½	.08½	.07½

* Resale or Imported (not an American maker's price).

ORGANIC CHEMICALS

	Oct. 1	Oct. 15	Jan. 1923
Acetanilide, U. S. P., bbls....lb.	.32	.32	.35
Acid, Acetic, 28 p. c.... 100 lbs.	3.38	3.38	3.17½
Glacial ....100 lbs.	12.78	12.78	12.05
Benzoic, U. S. P.........lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drums.............lb.	.28	.26	.32
50- to 110-lb. tins...lb.	.30	.28	.34
Citric, crystals, kegs.....lb.	*.50	*.50	*.48½
Oxalic, cryst., bbls., wks.lb.	.12	.12	.13½
Pyrogallic, resublimed...lb.	1.55	1.55	1.55
Salicylic, U. S. P.........lb.	.35	.35	.45
Tannic, U. S. P., bbls....lb.	.83	.83	.70
Tartaric, cryst., U. S. P...lb.	*.32	*.32	*.32
Acetone, drums.............lb.	.25	.25	.21
Alcohol,denatured, complete. gal.	.46	.46	.45
Ethyl, 190 proof, bbls...gal.	4.75	4.75	4.70
Amyl Acetate.............. gal.	4.50	4.50	2.50
Camphor, Jap, refined, cases .lb.	.87	.86	.86
Carbon Bisulfide, c/1........lb.	.06	.06	.06
Tetrachloride...........lb.	.10½	.10½	.10½
Chloroform, U. S. P., drums..lb.	.35	.35	.35
Creosote, U. S. P............lb.	.40	.40	.40
Cresol, U. S. P..............lb.	.25	.25	.25
Dextrin, corn ....100 lbs.	3.64	4.09	3.09
Imported Potato........lb.	.07½	.07½	.09
Ether, U. S. P., 100 lbs.......lb.	.13	.13	.13
Formaldehyde, bbls..........lb.	.12½	.12	.16
Glycerol, dynamite, drums...lb.	.16	.16	.16½
Methanol, pure, drums......gal.	1.05	1.05	1.35
Methylene Blue, med........lb.	2.25	2.25	2.25
Petrolatum, light amber......lb.	.04½	.04½	.03¾
Pyridine ....gal.	5.50	6.00	2.75
Starch, corn, pow'd.....100 lbs.	3.44	3.69	2.47
Potato, Jap.............lb.	.06	.06	.06¾
Sago...................lb.	.05	.05	.03½



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Oct. 1	Oct. 15	Jan. 1923
Beeswax, pure, white.........lb.	.38	.36	.36
Castor Oil, No. 3............lb.	.13	.13	.13
Ceresin, yellow..............lb.	.08	.08	.08½
Corn Oil, crude, tanks, mills...lb.	.10⅛	.08¾	.09¾
Cottonseed Oil, crude, f. o. b. mill....................lb.	.10	.09	.09⅝
Linseed Oil, raw, lc/l........gal.	.90	.95	.87
Menhaden Oil, crude, mills...gal.	.47½	.50	.53
Neat's-foot Oil, 20°..........lb.	.16¾	.16½	.18½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	5.95	5.85	6.25
Rosin Oil, first run..........gal.	.45	.45	.45
Shellac, T. N................lb.	.62	.62	.80
Sperm Oil, bleached winter, 38°....................gal.	.99	.99	1.03
Stearic Acid, double pressed...lb.	.13¼	.13¼	.12½
Tallow Oil, acidless...........lb.	.09½	.10¼	.11½
Turpentine, spirits of........gal.	1.00	1.03	1.56

METALS

	Oct. 1	Oct. 15	Jan. 1923
Aluminium, No 1, ingots.....lb.	.25	.25	.23
Antimony, ordinary......100 lbs.	6.75	6.75	6 75
Bismuth.....................lb.	2 75	2.75	2.75
Copper, electrolytic..........lb.	.13⅜	.12⅞	.14¾
Lake..................lb.	.13½	.13	.14¾
Lead, N. Y..............100 lbs.	6.65	6.60	7.80
Nickel, electrolytic...........lb.	.29	.29	.36
Platinum, refined, soft........oz.	116.00	116.00	118.00
Quicksilver, flask......75 lbs. ea.	61.00	61.00	73.00
Silver, foreign...............oz.	.65¼	.63¼	.63
Tin........................lb.	.42⅛	.41¼	.39
Tungsten Wolframite....per unit	8.50	8.50	7.50
Zinc, N. Y..............100 lbs.	6.65	6.65	8.25

FERTILIZER MATERIALS

	Oct. 1	Oct. 15	Jan. 1923
Ammonium Sulfate, expt.100 lbs.	3.45	3.45	3.90
Blood, dried, f. o. b. N. Y...unit	4.00	4.00	4.70
Bone, 3 and 50, ground, raw..ton	25.00	25.00	28.00
Calcium Cyanamide, unit of ammonia..................	2.25	2.25	2.25
Fish Scrap, dried, wks.......unit	4.00	4.00	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.25	3.25	3.00
Florida, 70%...........ton	3.55	3.55	3.55
Florida, 74–75%........ton	4.50	4.50	4.50
Tennessee, 72%.........ton	5.50	5.50	5.25
Potassium Muriate, 80%....unit	.68	.68	.68
Tankage, high-grade, f. o. b. Chicago...............unit	3.65 & .10	3.65 & .10	4.75 & .10

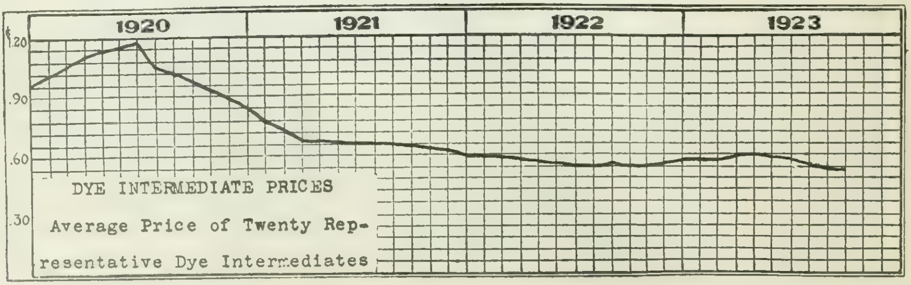
COAL-TAR CHEMICALS

Crudes

	Oct. 1	Oct. 15	Jan. 1923
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.25	.24	.30
Naphthalene, flake...........lb.	.07	.07	.06½
Phenol, drums...............lb.	.28	.26	.32
Toluene, pure, tanks.........gal.	.27	.26	.30
Xylene, 2 deg. dist. range, drums..................gal.	.55	.50	—

Intermediates

	Oct. 1	Oct. 15	Jan. 1923
Acids:			
Anthranilic..............lb.	.96	.96	1.10
Benzoic, tech............lb.	.70	.70	.65
Cleve's.................lb.	1.00	1.00	1.25
Gamma.................lb.	1.70	1.70	1.85
H......................lb.	.75	.75	.80
Metanilic...............lb.	.60	.60	.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.62	.62	.60
Nevile & Winther's.......lb.	1.10	1.10	1.15
Picric..................lb	.25	.25	.20
Sulfanilic...............lb.	.20	.20	.19
Tobias'.................lb	1.10	1.10	1.30
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil..................lb.	.16½	.16½	.17
Aniline Salt.................lb.	.24	.24	.25
Anthraquinone (sublimed).....lb.	1.30	1.30	1.30
Benzaldehyde, tech..........lb.	.75	.75	.65
U. S. P.................lb.	1.50	1.50	1.40
Benzidine Base..............lb.	.82	.82	.84
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol..............lb.	3.80	3.80	3.75
Dianisidine.................lb.	4.60	4.60	4.50
p-Dichlorobenzene...........lb.	.17	.17	.17
Diethylaniline...............lb.	.60	.60	.60
Dimethylaniline.............lb.	.41	.41	.41
Dinitrobenzene..............lb.	.19	.19	.19
Dinitrotoluene..............lb.	.19	.19	.20
Diphenylamine..............lb.	.48	.48	.50
G Salt.....................lb.	.55	.55	.60
Hydroquinol................lb.	1.25	1.25	1.05
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.22	.22	.26
a-Naphthylamine............lb.	.35	.35	.29
b-Naphthylamine............lb.	.75	.75	.95
m-Nitroaniline..............lb.	.78	.78	.80
p-Nitroaniline...............lb.	.74	.74	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol..............lb.	.75	.75	.72
o-Nitrotoluene..............lb.	.09	.09	.10
p-Nitrotoluene..............lb.	.50	.50	.65
m-Phenylenediamine.........lb.	.96	.96	1.00
p-Phenylenediamine.........lb.	1.45	1.45	1.50
Phthalic Anhydride..........lb.	.25	.25	.35
R Salt.....................lb.	.55	.55	.55
Resorcinol, tech.............lb.	1.40	1.40	1.50
U. S. P.................lb.	2.25	2.25	2.00
Schaeffer's Salt.............lb.	.60	.60	.60
Sodium Naphthionate........lb.	.62	.62	.62
Thiocarbanilide..............lb.	.35	.28	.35
Tolidine (base)..............lb.	.95	.95	.95
Toluidine, mixed............lb.	.31	.31	.30
o-Toluidine..................lb.	.18	.18	.15
p-Toluidine..................lb.	.90	.90	1.00
m-Toluylenediamine..........lb.	.90	.90	.95
Xylidine....................lb.	.50	.50	.42



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EDITORIALS

Classified Membership

When the Committee on Progress in Society Procedure was appointed, one of the topics for its consideration was enhancing the value of membership in the American Chemical Society, perhaps through some classification of membership. After due consideration and at the suggestion of the original committee, the matter was referred to a special committee, which made a report of progress at the Milwaukee meeting. It is expected that a final report will be presented at Washington. If the committee is to consider the views held by various members of the Society, it is obvious that these views must be forwarded promptly.

When the question was brought before the Council at Milwaukee several diverse opinions were expressed. There are many who look upon the great success of the American Chemical Society under its present scheme of organization and membership as sufficient evidence that it would be well to make no change. The men who hold this view are, for the most part, those who have made their mark, are known for what they have accomplished, and would benefit little, if any, by the introduction of a membership classification. Another view, held perhaps by men who are arriving in the profession, is that a group should be formed admission to which would be under specifications clearly indicating marked attainment in the chemical profession. The requirements for admission would obviously be high, and perhaps beyond those which qualify a candidate for admission to the class of "Fellow" in several existing organizations. Membership in such a group would be a distinction for which chemists would be glad to strive. Still another view is that expressed by the younger men who desire membership in the American Chemical Society to indicate chemical training and experience and more than an active interest in chemistry. These men would distinguish between those who are practicing chemistry or who have a knowledge of chemistry and those who now become members of the Society either for the encouragement of the science or for the many benefits which the Society affords. They hold that "member of the American Chemical Society" is a designation which should be reserved for those qualified by their training or experience for the practice of chemistry, and that interested nonchemists would be just as well pleased to be known as "subscribing members."

Granting for the sake of argument that, having accomplished our present success under a highly democratic organization, it is now time to make changes to meet changed conditions, the question becomes—which, if any, of these ideas should prevail? Having suggested that those who have views should express them to the committee, we express ours in the hope that many will come forward with improvements.

First of all, whatever is done should not be retroactive, and those who are now members of the American Chemical Society should continue as such without any discrimination. Secondly, we believe that there should be written into the requirements for membership in future a specification calling for chemical training, experience, or actual participation in chemical work, such that the value of membership will be prized and surrendered with reluctance. A certificate might be issued stating that the holder had satisfied specific requirements and in consequence had been made a member of the Society. To provide for those who do not aspire to this membership, provision should be made for a class of subscribing members who would not receive such certificates, but who would receive the journals and have affiliation with local sections. Then, provision should be made for a class of distinguished chemists, called for the want of better designation "Fellows of the American Chemical Society." There are those who do not like this phrase, and perhaps a much better one can be found, but the point we desire to stress is that membership in this group should at once indicate unquestioned attainment in the profession of chemistry. Perhaps not more than five or ten per cent of our present membership could qualify, but having written requirements for admission into this group and then having created an impartial, small committee to measure a man's accomplishments against these requirements, it should not be difficult to make election to this group of Fellows something which any chemist in America would welcome and prize as a high honor.

By this plan we believe the value of membership in the American Chemical Society would be greatly enhanced, that the democratic spirit of our present organization would not be disturbed, and that a long step would be taken in meeting present-day requirements.

Executive committees of sections should discuss the problem and express their views. Those suggestions which represent the sentiment of a section should be officially transmitted. Individual opinions are also wanted. If you have a better plan or wish to discuss the one here set forth, address your letters to William Hoskins, 111 West Monroe St., Chicago, Ill., who is chairman of the committee, or send them to the editor of This Journal, who will be glad to forward all communications promptly to the committee.

Engineering Education and American Industry

The National Industrial Conference Board in Special Report No. 25, under the above title, presents the conclusions of a group of skilled and experienced men on a subject of interest to all chemists. The report is the joint work of the board with a committee from the Society for the Promotion of Engineering Education, and it shows clearly the interrelationship between the engineering schools and the industries as well as the need for coöperation between these groups if success is to follow the effort to develop industrial leaders. The report is summarized as follows:

> 1—There is a rapidly growing need for administrative and technical ability in practically all lines of activity. This is especially true of the manufacturing and mechanical industries.
>
> 2—There is an increasing demand for graduates of engineering schools to enter upon work which will fit them for positions of administrative as well as technical responsibility. This, apparently, is because courses of education in engineering and applied sciences have been highly successful in the early development of both kinds of talent.
>
> 3—The demand for young men with capacity for becoming administrative or technical leaders is already far greater than the number of such men now being graduated from the engineering schools.
>
> 4—It is, nevertheless, more important that a greater proportion of the graduates of engineering schools be young men of high quality than that the total number of graduates be increased. Therefore, admission to these schools should be based

on selective tests for fitness, intelligence, and character as well as for knowledge.

5—The preparatory schools can perform a great service to industry as well as to the students by properly evaluating the advantages of the engineering schools and guiding toward those schools the boys who have, or in whom can be developed, an interest in producing things. Such boys should develop into industrialists.

6—There is a growing opinion that the engineering schools should provide a thorough grounding in fundamentals of engineering and applied sciences, rather than specialized training. Such a grounding is best accomplished when accompanied by actual contact with industry as well as by work in classroom and laboratory.

7—There should be more and better training courses in connection with industrial establishments to supplement the educational courses of the colleges.

8—Close coördination of educational effort between industrialists and educators is therefore necessary to meet the need for leaders.

Reorganization of Executive Departments

IT WILL be recalled that the reorganization of the executive departments of the Government has been a question under discussion for some months and that the plan submitted by a joint committee had the approval of the late President. There are many features of the plan which do not appeal to certain Cabinet officers and those who dislike to see a bureau transferred from one department to another, no matter how logical that may be. There has been particular opposition to the proposed consolidation of the War and Navy Departments under a single Cabinet officer in a new department known as the Department of Defense. There are, however, some features of the reorganization plan to which there is no such opposition and concerning which action should be taken at once.

One is to reduce the routine work which heretofore has been a part of the President's duty. It is recommended that he be provided with a secretary as at present, and with an executive secretary who would have charge of four assistants. One of these would be responsible for the personnel to deal with patronage; another would keep the President informed as to the progress of bills in both houses of Congress and, in turn, advise the Congress of the President's wishes in matters of legislation; a third would advise the President of public opinion as reflected by the press; and the fourth would be in charge of applications for clemency and prepare the facts upon which the President could take action.

Another step in reorganization which should be taken at once concerns the Department of the Interior. For some time the engineers, in particular, have advocated the creation of a Department of Public Works, and that portion of the reorganization plan which deals with the Department of the Interior embraces many of the essential features proposed by the engineers. At a recent meeting of the Executive Board of the Federated American Engineering Societies, preliminary steps were taken to hold a conference on the subject in Washington, January 9, 1924, and to urge Congress to put the plan into effect.

About two hundred technical and allied organizations have been invited to send delegates to this conference. Meanwhile, a bill authorizing the reorganization of the Department of the Interior in accordance with the provisions noted below and including an Assistant Secretary for Public Works will be prepared and introduced in Congress. As proposed, the new Department of the Interior would have the following organization (the words in parentheses designating the present connections of certain groups not now in the Interior Department):

SECRETARY OF THE INTERIOR
Executive Offices

ASSISTANT SECRETARY FOR PUBLIC DOMAIN
- Administration of Alaska and Hawaii
- Indian Lands and Reservations
- General Land Office
- Geological Survey
- War Minerals Relief Commission
- National Park Service
- National Military Park Commissions (War)
- Federal Power Section (Federal Power Commission)

ASSISTANT SECRETARY FOR PUBLIC WORKS
- Bureau of Public Roads (Agriculture)
- Supervising Architect's Office (Treasury)
- Alaskan Engineering Commission
- Reclamation Service
- Board of Engineers for Rivers and Harbors (War)
  - Board of Engineers, New York City (War)
  - United States Engineer Offices (War)
  - Mississippi River Commission (War)
  - California Debris Commission (War)
- Board of Road Commissioners for Alaska (War)
- Bureau of District of Columbia Buildings and Grounds
  - Office of Public Buildings and Grounds (War)
  - Commission of Fine Arts (Independent)
  - Superintendent State, War, and Navy Department Buildings (Independent)
  - Architect of the Capitol (Congress)
  - Rock Creek and Potomac Parkway Commission (Independent)

SOLICITOR (Justice)

Purchase and Sale of Degrees

THE AMERICAN CHEMICAL SOCIETY has played an active part in the effort to make impossible the selling of academic degrees by those who claim to represent reputable American universities. One of the greatest offenders has been the Oriental University, with headquarters in Washington, and our readers will rejoice to hear that the Post Office Department has issued a fraud order against the Oriental University and H. P. Holler, its president. In his report to the Postmaster General recommending the issuance of the order, the Acting Solicitor declared that the evidence in the case showed that "this is a scheme for obtaining money through the mails by means of false and fraudulent pretenses, representations, and promises."

But there are other groups which also need official notice. They are to be found in various parts of the country and, as they operate principally in foreign countries, it seems necessary for our technical journals again to state that *no reputable educational institution offers degrees for sale.*

From England we have notices and correspondence offering any degree which may be desired by the University of the Trinity College, Chicago, Ill., and the Lincoln-Jefferson University of the same city. The advertising matter describes the colors and materials of which the hoods for the various degrees are made, and while it is claimed that degrees are awarded only upon merit, this is largely offset by the statement, "in special cases a thesis consisting of about seven thousand five hundred words on a subject chosen with the consent of the faculty concerned is accepted from candidates." Neither of these institutions is listed in any educational directory nor in the telephone directory of the city, and inquiries sent to the address given have failed to secure response.

Not to be outdone by the Middle West, the Far West has a similar institution at Highland Park, Los Angeles, Calif., and advertises in Italy through an agent in Venice. This is called the American University. The main office, headquarters, and campus consist of a small upstairs room, which also serves as the living, sleeping, and office quarters of the "dean." The principal furnishings of the "university" are a dilapidated bed, an aged desk, and a couple of chairs, which harmonize perfectly. This alleged university offers to confer doctor and engineer degrees and the title of professor, and to issue diplomas to accountants.

Those who operate these spurious institutions cannot always be apprehended. Surely few fail to realize that in purchasing a degree they are endeavoring to acquire a distinction which to be genuine must be obtained by a far more arduous proceeding. It is therefore not easy to prove that the purchaser has been defrauded. To show that he who purchases does so with the intent of defrauding others would be a simpler matter. It is somewhat like a case where a man was tried for selling loaded dice and marked playing cards. He was able to prove that he sold these devices for just what they were—those who were to be sued for fraud were his purchasers, not himself.

However, action can proceed along other lines, as in the case of the Oriental University. This "university" advertised a dean and numerous professors in each of several so-called colleges, claiming a total of forty-seven resident professors in the "faculty." The nonexistence of any faculty in the true sense of the word and the finding that the so-called "faculty" functioned principally in inducing persons to become students and remit the necessary fee was sufficient ground for issuing the fraud order.

We give publicity to these facts as they come to us, in the hope that no one will allow himself to be deceived by any of these devices.

Parallels

READ the following panegyric on Athens by Pericles recorded by Thucydides, II, 37, translated by Jowett, and quoted from "The Greek View of Life," by G. L. Dickinson:

> Our form of government does not enter into rivalry with the institutions of others. We do not copy our neighbours, but are an example to them. It is true that we are called a democracy, for the administration is in the hands of the many and not of the few. But while the law secures equal justice to all alike in their private disputes, the claim of excellence is also recognized; and when a citizen is in any way distinguished, he is preferred to the public service, not as a matter of privilege, but as the reward of merit. Neither is poverty a bar, but a man may benefit his country whatever be the obscurity of his condition. There is no exclusiveness in our public life, and in our private intercourse we are not suspicious of one another, nor angry with our neighbour if he does what he likes; we do not put on sour looks at him, which, though harmless, are not pleasant. While we are thus unconstrained in our private intercourse, a spirit of reverence pervades our public acts; we are prevented from doing wrong by respect for authority and for the laws, having an especial regard for those which are ordained for the protection of the injured, as well as for those unwritten laws which bring upon the transgressor of them the reprobation of the general sentiment.
>
> And we have not forgotten to provide for our weary spirits many relaxations from toil; we have regular games and sacrifices throughout the year; at home the style of our life is refined; and the delight which we daily feel in all these things helps to banish melancholy. Because of the greatness of our city the fruits of the whole earth flow in upon us, so that we enjoy the goods of other countries as freely as of our own.
>
> Then again, our military training is in many respects superior to that of our adversaries. Our city is thrown open to the world, and we never expel a foreigner or prevent him from seeing or learning anything of which the secret if revealed to an enemy might profit him. We rely not upon management and trickery, but upon our own hearts and hands. And in the matter of education, whereas they from early youth are always undergoing laborious exercises which are to make them brave, we live at ease, and yet are ready to face the perils which they face.
>
> If then we prefer to meet danger with a light heart but without laborious training, and with a courage which is gained by habit and not enforced by law, are we not greatly the gainers? Since we do not anticipate the pain, although when the hour comes, we can be as brave as those who never allow themselves to rest; and thus too our city is equally admirable in peace and in war. For we are lovers of the beautiful, yet simple in our tastes, and we cultivate the mind without loss of manliness. Wealth we employ, not for talk and ostentation, but when there is a real use for it. To avow poverty with us is no disgrace; the true disgrace is in doing nothing to avoid it. An Athenian citizen does not neglect the state because he takes care of his own household; and even those of us who are engaged in business have a very fair idea of politics. We alone regard a man who takes no interest in public affairs, not as a harmless, but as a useless character; and if few of us are originators, we are all sound judges of a policy. The great impediment to action is, in our opinion, not discussion but the want of that knowledge which is gained by discussion preparatory to action. For we have a peculiar power of thinking before we act, and of acting too, whereas other men are courageous from ignorance but hesitate upon reflection. And they are surely to be esteemed the bravest spirits who have the clearest sense both of the pains and pleasures of life, but do not on that account shrink from danger.
>
> To sum up, I say that Athens is the school of Hellas, and that the individual Athenian in his own person seems to have the power of adapting himself to the most varied forms of action with the utmost versatility and grace. This is no passing and idle word, but truth and fact; and the assertion is verified by the position to which these qualities have raised the state. For in the hour of trial Athens alone among her contemporaries is superior to the report of her. No enemy who comes against her is indignant at the reverses which he sustains at the hands of such a city; no subject complains that his masters are unworthy of him. And we shall assuredly not be without witnesses; there are mighty monuments of our power which will make us the wonder of this and of succeeding ages; we shall not need the praises of Homer or of any other panegyrist, whose poetry may please for the moment, although his representation of the facts will not open a path for our valour, and have everywhere planted eternal memorials of our friendship and of our enmity.

In how many ways is this parallel and similar to orations which for a hundred years have been delivered about our own country? Many of these characteristics of ancient Athens are really applicable to the United States, but it is well to pause and question—what are we doing to avoid making applicable to America the comments of Mr. Dickinson upon the later trend of Athens when he says:

> An impression so superb as this it is almost a pity to mar with the inevitable complement of disaster and decay. But our account of the Athenian polity would be misleading and incomplete if we did not indicate how the idea of equality, on which it turned, defeated itself, as did, in Sparta, the complementary idea of order, by the excesses of its own development. Already before the close of the fifth century, and with reiterated emphasis in the earlier decades of the fourth, we hear from poets and orators praise of a glorious past that is dead, and denunciations of a decadent present. The ancient training in gymnastics, we are told, the ancient and generous culture of mind and soul, is neglected and despised by a generation of traders; reverence for age and authority, even for law, has disappeared; and in the train of these have gone the virtues they engendered and nurtured. Cowardice has succeeded to courage, disorder to discipline; the place of the statesman is usurped by the demagogue; and instead of a nation of heroes, marshaled under the supremacy of the wise and good, modern Athens presents to view a disordered and competitive mob, bent only on turning each to his own personal advantage the now corrupt machinery of administration and law.

Let us take stock. Are we threatened with a repetition of the experience of this nation, now far past its perihelion? Do we give such attention to the lessons of history as to realize that we move in cycles and are often threatened by the same rocks that have wrecked other ships of state? Are we Americans wise and strong enough to right our course before we are destroyed?

Two Things To Remember—Place your Christmas order with Alexander Williams, Jr., 67 Wall St., New York, N. Y., for a set of the books which are being distributed in connection with the Prize Essay Contest. These books are offered SOCIETY members at the actual cost of publication, $2.50 for the five volumes.

Make your hotel reservations for the Washington meeting!

SYMPOSIUM ON BREAD

Papers presented before the Joint Session of the Division of Industrial and Engineering Chemistry and the Division of Agricultural and Food Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

Variations in Wheat Types

Some Causes and Effects

By **L. A. Fitz**

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WHEAT, rye, and barley are included in the tribe of the grass order called *Hordeae.* Wheat and rye are still more definitely located in the subtribe, *Triticeae.* There are in cultivation eight groups of wheat generally recognized with botanical names and relative ranks, according to Hackel, as follows:

- *Triticum*
  - *monococcum, Linn*, einkorn or one-kerneled wheat
  - *sativum, Lam.*
    - *dicoccum, Schr.*, emmer.
    - *spelta, Linn.*, spelt
    - *tenax*
      - *vulgare, Vill.*, common wheat
      - *compactum, Host.*, club wheat
      - *turgidum, Linn.*, poulard wheat
      - *durum, Desf.*, durum wheat
  - *polonicum, Linn.*, Polish wheat

We are interested principally in the common and the durum wheats.

From the beginning of botanical classification there was a tendency to regard different forms of wheat as distinct species. Later writers adopted a more reasonable view and have recognized comparatively few species, but the subdivisions of *Triticum vulgare* are regarded as varieties.

Wheat grown in the United States shows a great diversity of type. This is but natural since wheat has been grown in all the forty-eight States, which covers a wide range of environmental conditions. There are at least two hundred distinct varieties known. Some of these are of local adaptation, while others have wide adaptation. This adaptation is an important factor as it affects yield, and consequently, profits. Hence the choice of variety is important and is given careful consideration by the growers.

Classification

"Classification of American Wheat Varieties," by Ball and Clark[1] is the best and most recent work dealing with this subject. The classifications made are based on much painstaking work, including over twenty-five thousand plantings in classification nurseries in widely separated portions of the United States. The bases of classification are morphological and physiological characters. Under the former are included plant, stem, spike, glume, shoulder, beak, awn, kernel, germ, crease, cheek, and brush characters, while under the latter or physiological characters are productivity, milling and bread-making value, resistance to low temperature, and resistance to disease.

The classification of commercial wheats based on kernel characteristics divides the market wheat into five great classes or types—namely, hard red spring, durum, hard red winter, soft red winter, and white wheat. The first four classes are further divided into three subclasses each, the percentage of hard and vitreous kernels being the basis of subdivision in the hard wheats. Each subclass is still further divided into six grades, including sample, the basis for separation into grades being quality, condition, mixture or foreign material, and test weight. Some attention is given to kernel characters, but comparatively little to the physiological characters of milling and baking quality, except as these may inadvertently be involved in the subclass and in the numerical grade assigned on account of quality, condition, mixture, or foreign material, and test weight.

We are interested primarily in the milling and baking or the bread-making values of these wheats. The ultimate relative market value of these wheats depends upon the estimation of milling and baking value after making certain physical and chemical tests.

There are a large number of varieties included under each class of wheat. Some of these varieties are well known throughout the whole section producing wheat of this class; other varieties are known only locally.

Hard Red Spring Wheat—Of the hard red spring varieties, Fife and Bluestem have been perhaps best known and most widely distributed, but are now being rapidly displaced by Marquis. The Fife wheat of this country dates back to 1842, when David Fife, of Otonabee, Ont., received from a friend in Glasgow, Scotland, a small package from a shipload arriving from Danzig, Germany, but supposedly of Russian origin. Later investigation indicated that the wheat originally came from Galicia. There have been many synonyms, such as Red Fife, Scotch Fife, Canadian Fife, Powers Fife, Wellman's Fife, etc. It is a hard red spring wheat with a short kernel having a wide, deep crease.

A number of different varieties of wheat have borne the name Bluestem, but the particular one referred to in the Dakotas and Minnesota is a hard red spring wheat with glumes pubescent and kernels narrower and longer than Fife. It shows excellent milling and baking qualities.

Marquis is of hybrid origin, a cross between Hard Red Calcutta and Red Fife, made by William Saunders. It is a high yielding, early maturing variety of the Fife type, and one of our best varieties when judged from the milling and baking standpoint.

Hard Red Winter Wheat—In the hard red winter wheat class, the varieties Turkey, Kharkov, and Kanred are best known and most widely distributed. Turkey was brought into south-central Kansas in the early seventies by the Russian Mennonite settlers. The plant is very winter-hardy and drought-resistant, giving good yields. The kernels are long, hard, dark red with tight crease. This variety is especially prized for its high milling and baking value.

The Kharkov variety was probably originally identical with the Turkey, although it comes from the province or government of Kharkov, about two hundred miles further north than Crimea, the original home of the Turkey.

Kanred is quite similar to Turkey, but somewhat more winter-hardy and rust-resistant. It is the product of a single head selection from the Crimean variety, made in 1906 by H. F. Roberts, of the Kansas Agricultural Experiment Station. Samples of Kanred and Turkey grown under the same conditions have been subjected to milling and baking tests, with practically identical average results. It may be interesting to note here that John H. Parker, of the Kansas Agricultural Experiment Station, has made some crosses between Kanred and Marquis which are very promising. If he has succeeded in combining the good qualities of both varieties so as to secure an early, rust-resistant, high-yielding wheat with the best of milling and baking qualities, such result will be a real and worth-while achievement.

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[1] *U. S. Dept. Agr., Bull.* **1074.**

Soft Red Winter Wheats—The soft red winter wheats have been most widely known through such varieties as Fultz, Fulcaster, Mediterranean, and later varieties such as Jones' Winter Fife, Mealy, and Harvest Queen. These varieties, like those of the hard wheats, represent both bearded and beardless types. The chief difference between the hard and soft wheats is the difference in texture of kernel. The endosperm of typical kernels of soft wheat is entirely soft and mealy or starchy, while that of typical kernels of hard wheat is hard and horny or vitreous throughout. However, each class produces wheats which approach the other class until there is an overlapping in kernels that are semi-hard.

White Wheats—The white wheats are quite widely distributed throughout the United States, and are represented by a large number of varieties, some of the most important being White Australian (also known as Pacific Bluestem), Dawson's Golden Chaff, Gold Coin, Defiance, Big Club, and Little Club. A large number of the wheats of the Pacific coast and the intermountain area belong to the white wheat class. These white kerneled varieties are easily distinguished from the red wheats by their appearance, and also, as a rule, possess lower milling and baking qualities.

Durum Wheats—The durum varieties belong to a class distinctly different from the common bread wheats. The plants all have the spring habit of growth, the leaves have larger, broader blades, and the spikes are compact and very heavily bearded or awned. When true to type the kernels are very hard and horny. In all but a few red varieties the typical kernels are clear or translucent and generally referred to as amber colored.

The durum wheats have been widely grown in the United States only during the last twenty years, and on account of their drought-resistant qualities are particularly adapted to the arid portions of the western spring wheat States. The two best known and most widely distributed varieties are Arnautka and Kubanka.

Variations in Wheat

From the wheats belonging to the five great classes, the miller selects and blends until the mixture going to his rolls will produce a type of flour that will satisfy his customers, and his big problem is, once he has his product established, to maintain a uniform quality from day to day and week to week throughout the year. This is no easy task because of both physical and chemical variations in his raw product. He has to contend with varietal differences within a given area and, what is usually more important, he must deal with differences within a given variety due to climatic and soil conditions.

In some States, such as Ohio or Pennsylvania, the variations in climatic conditions will not be great and the varietal differences will be more manifest. In States like North Dakota or Kansas, where the rainfall may vary from over 30 inches in the eastern to less than 19 inches in the western part and the altitude also increases as the rainfall decreases, the variations in composition due to climatic difference far exceed those due to variety.

Variation in Protein Content—The amount of protein in relation to carbohydrates is the factor showing greatest variation and, as this corresponds very closely to the amount of gluten, it is a most important factor. The soft red winter wheats and the white wheats, each considered as a class, average considerably lower in protein than the hard red wheats or the durum wheats, the usual range being from about 7 to 11 per cent in the soft wheats, while the hard wheats may contain anywhere from 8.5 to over 23 per cent. A limited amount of rainfall with some hot winds during the latter part of the fruiting period results in failing to store sufficient carbohydrate material to produce a plump kernel; hence the resulting kernel is shriveled, of low test weight and low flour yield, but high in gluten content. Usually this gluten is of good quality, strong yet elastic, but sometimes it is tough and inelastic, or at other times it is sticky or runny. Usually the quantity of wheat having good quality of gluten is rather limited and the miller must resort to blending wheats with glutens of opposite qualities in an effort to produce a blend that will have gluten satisfactory in quality and quantity.

Yellow-Berry—While different lots of hard winter wheat consisting wholly of hard and vitreous or flinty kernels may show considerable difference in protein content, a more marked difference is usually shown by the soft, mealy, or partially soft kernels known as "yellow-berry" hard wheat. It is also true that such wheat is lacking more in quality than in quantity of gluten.

Hackel, in describing the yellow-berry conditions, says:

> If the albuminoids so fill up the intervals between the starch grains that the latter seem to be imbedded in cement, the albumin appears translucent and the fruit is called corneous; but if the union is less intimate, there remain numerous small air cavities and the albumin is opaque and the fruit is mealy. Both conditions may occur in the same variety of wheat.

The yellow-berry, then, appears to be a distinctly physiological growth product due to certain conditions thus far not clearly analyzed nor satisfactorily explained. Authorities, after many years' investigation into the causes of yellow-berry and means of prevention, do not agree. It seems quite probable that there are many contributing factors causing yellow-berry and that under certain conditions a single factor may be the controlling one, while under different conditions the effect of this particular factor is not recognizable.

Le Clerc and Yoder[2] in their triangular experiments demonstrated that climate has a much greater influence than soil upon the percentage of yellow-berry and upon the chemical composition.

Headden[3] states that his experiments did not substantiate the claim sometimes made that climatic conditions favorably influence the development of or cause yellow-berry. On the other hand, he states that yellow-berry can be very much lessened or entirely prevented by the application of a sufficient quantity of available nitrogen; that yellow-berry can be greatly intensified or increased by the application of available potassium; that yellow-berry is not indicative of an exhausted soil; that the presence of yellow-berry indicates that potassium is present in excess of what is necessary to form a ratio to the available nitrogen present, advantageous to the formation of a hard, flinty kernel; furthermore, that yellow-berry is under the control of the grower. If there should be sufficient difference in the price of grain produced, he could control it with a margin of profit.

These conclusions were drawn from a comparatively limited number of experiments carried on in the State of Colorado. Whether or not these principles can be applied throughout the country seems somewhat doubtful.

Experiments carried on at the Kansas Agricultural Experiment Station show that the per cent of yellow-berry and composition of the seed wheat have no effect upon the per cent of yellow-berry or the protein content of the resulting crop; furthermore, that proper crop rotation and proper seed-bed preparation have a beneficial effect upon milling and baking value of the wheat; and that apparently some varieties are more resistant to the common factors which usually result in increased percentage of yellow-berry.

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[2] *J. Agr. Research*, **1**, 275 (1914).

[3] Colo. Agr. Expt. Sta., *Bull.* **205**.

It is probably not necessary to state that crop rotation and proper seed-bed preparation bring sufficient yield increase to pay several times the additional cost of production, even though an improvement in milling and baking quality were not secured.

Flour Manufacture

By C. H. Bailey

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THE success of the roller milling process is dependent upon the fact that substantial differences exist in the physical properties of the several wheat kernel structures. Thus, the branny covering of the berry is distinguished by its tough, fibrous character. The germ, or embryo, is rich in fats and oils, and hence tends to flake when crushed between rollers. The endosperm, or floury portion, on the other hand, is friable and tends to fracture when struck. It is impossible, however, to effect a quantitative separation of the various kernel structures in roller milling. Small quantities of the fibrous bran and the oily germ find their way into the flour, and particularly into the low or clear grades. A substantial proportion of endosperm or floury material is likewise to be found in the by-products, bran and middlings. Commercial bran not infrequently contains 15 to 20 per cent of flour, while commercial standard middlings are often found to contain 30 per cent or more of flour. It accordingly follows that, of the 82 to 85 per cent of endosperm (potentially flour) to be found in the average plump wheat kernel, not to exceed 72 to 75 per cent of the kernel is separated in the form of straight grade flour.

In the modern roller mill the first important process is cleaning and conditioning the grain. Commercial wheat frequently contains a considerable quantity of foreign matter, including weed seeds, sticks, stones, fragments of straw, etc. An effort is made to separate these from the wheat as completely as possible before the latter is ground. Northwestern grown hard spring wheat contains more of this foreign matter or dockage than does any other class of American wheat, and a variety of cleaning appliances are necessary to the separation of the foreign matter in this wheat. Certain of the weed seeds, which are most difficult of separation, are of interest to the chemist because of constituents which they contain. Thus the seed of the corn cockle, *Agrostemma githago*, contains a saponin which is reported to be somewhat toxic. The seed of the wild vetch, *Vicia angustifolia*, is very yellow, owing to the carotinoid pigments which it contains, and a cyanogenetic glucoside found in this seed yields hydrocyanic acid and benzaldehyde when treated with warm water. If wild vetch seed is present in wheat in excess of 1 per cent at the time of milling, the characteristic odor of benzaldehyde will be observed in the dough when the flour is mixed with water. Seeds of the giant ragweed, commonly known as "king heads" in the grain trade, if present in wheat at the time it is ground, result in flour of less desirable properties. It is accordingly necessary that such seeds be separated before attempting to grind the wheat.

The spores of bunt or stinking smut are frequently found in commercial grain, particularly from western areas, and relatively small amounts of this material will darken the flour appreciably. Several special treatments are resorted to in order to remove these smut spores, including scouring with bolted air-slacked lime, and washing with liberal quantities of water. In the latter event special machinery must be available for "whizzing" the wheat in a centrifugal drier to remove the excess of water.

It is a common practice to add appreciable quantities of water to dry wheat before grinding, in an effort to enhance the toughness of the branny covering. This water may be added in the wet washing process or may be sprayed upon the grain in what is commonly known as the tempering process. Frequently, cold wheat is warmed slightly before the tempering water is added. The moistened grain is held for a few hours in order that the bran may absorb the added water, but the period is so adjusted that no substantial penetration of the water into the endosperm results.

The cleaned and tempered wheat is then crushed by passing it between corrugated steel rollers. The individual rollers of the pair revolve at different rates of speed, the differential being commonly about 2.5 to 1. After the first breaking or crushing of the wheat, the resulting chop is bolted and the coarse material reground between another pair of corrugated break rolls. Five or six breaks are ordinarily provided in hard wheat mills, and after the last break the coarse material is known as bran.

In addition to the coarse fractions scalped from the break roll chop, two other classes of materials are separated on bolting this chop. The fine portion which will pass through a bolting silk is known as break flour, and is sprouted directly to the flour bins. Fragments intermediate in size between the coarse fraction and the flour are known as "middlings." These are further classified by passing them over a sieve in a machine known as a purifier, which effects a separation on the basis of size of particles. In addition, a fan at the top of the purifier box draws an air current through the sieves, which lifts out light, fibrous particles. The purified middlings are then ground between smooth steel rollers and the ground material is bolted to remove the fine particles of flour. Coarse fractions which failed to pass through the flour sieves are reground twice or three times. The flour produced by each regrinding of this material contains increasing proportions of fiber, ash, and soluble proteins, and becomes progressively darker in color. From this description of the process it is evident that a considerable number of flour streams will be found in a flour mill, one such stream resulting from each break and each middlings reduction. Not uncommonly twenty to twenty-five or more flour streams are thus available to the miller, and he may combine any or all of them to suit the demands of the trade.

While the individual flour streams may be bleached, the more common process when bleaching is resorted to is to treat the finished products with bleaching agents. The most common bleaching agents used in American mills are:

(1) Nitrogen peroxide, ordinarily generated in the mill by means of a flaming electric arc.

(2) Chlorine, which is usually purchased in a liquid form in steel drums, often mixed with small percentages of nitrosyl chloride. Chlorine is generated by the electrolytic process in a few mills. Occasionally, a double treatment with chlorine and anhydrous ammonia is resorted to.

(3) Nitrogen trichloride produced commercially by passing gaseous chlorine through a solution of ammonium sulfate.

(4) Benzoyl peroxide, added in mixture with acid calcium phosphate below the second break roll.

Numerous criteria of flour grades have been proposed by cereal chemists during the past half-century. Among these the following may be mentioned: (*a*) ash content, (*b*) pentosan content, (*c*) fat content, (*d*) fiber content, (*e*) titrable acidity of water extracts, (*f*) percentage of soluble proteins, (*g*) specific conductivity of water extracts, (*h*) buffer action of water extracts, (*i*) catalase activity, (*j*) relative proportion of branny particles, and (*k*) number of wheat hairs per unit of flour.

All the foregoing bear a negative correlation to the grade of flour—that is, the percentage or index increases with decreasing grade or degree of refinement and commercial value. In addition to the items mentioned, flour grade is generally correlated with the color or visual appearance of dry flour, of dough made therefrom, and of the baked bread. The appearance of the crumb of baked bread is extensively used in cereal laboratories as an index of flour grade. The color which results on wetting the flour is used in a crude way by millers and milling chemists in what is known as the Pekar test. This test has been made more or less quantitative by measuring the relative extent of color change per unit of time in the freshly wetted material.

Flour and Bread as Colloid Systems[1]

By Ross Aiken Gortner

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WHEAT flour, the only one of the cereal flours which is adapted to the manufacture of yeast-leavened bread, owes its desirable properties to the nature of the proteins of the wheat. These proteins have been extensively studied and comprise a prolamine *gliadin*, a glutelin *glutenin*, an albumin *leucosin*, a globulin, and a proteose.

The gliadin and glutenin are present in the dough in a rather intimate physical or physico-chemical mixture which is known as the gluten. Whether or not gluten is formed in the process of dough manufacture or whether it already exists in the endosperm of the wheat berry is still an open question.

The gluten plays its role in bread manufacture in that it absorbs water and forms an elastic gel, which stretches under the tension of the carbon dioxide produced by yeast fermentation and thus "raises" the loaf. The tenacity with which gluten particle adheres to gluten particle varies widely from flour to flour. Those flours which have a high ratio of carbon dioxide production to carbon dioxide diffusing through the gluten are desirable for bread-making purposes, and are known as "strong" flours. Those flours that form doughs which fail to retain a large proportion of the carbon dioxide are known as "weak" flours, and are more suited to the manufacture of pastry and crackers than to yeast-leavened bread.

Many investigators have concerned themselves with a study of the factors which may be involved in flour strength, but it has been only recently that the newer theories and methods of colloid chemistry have been applied. These studies give promise of assisting materially in a solution of the problem.[2]

The work referred to has convinced the writer that the physical properties of the gluten are, in many instances at least, the determining factor as to whether or not a given lot of flour will produce a satisfactory loaf of bread. It would appear that the physical properties of the gluten are in a large measure determined at the time the wheat proteins are laid down in the endosperm of the wheat berry, with the result that the strong flours are strong, not because they differ in acid or salt content from weak flours, but because the gluten is capable of forming a more tenacious gel than is the gluten from a weak flour. The question as to why glutens differ in tenacity is still unsolved. Nevertheless, the fact remains that such differences do occur. It would appear as if the flour strength problem were closely allied to the rubber problem. Why does rubber produced in different localities and by different methods differ so enormously in tensile strength and in value? It appears probable that rubber is a polymer of isoprene. It may be that chemically the rubbers are indistinguishable from each other, but this does not preclude a wide difference in physical properties. A solution of the rubber problem may solve the strong and weak flour question, and perhaps the cereal chemist may solve the problems vexing the rubber manufacturer. It is a long cry from bread to automobile tires; nevertheless, in this problem of tensile strength they meet on common ground.

In an investigation having for its object the question as to which of the proteins of wheat flour was responsible for the variation in the physical properties of the gluten, it was found[3] that the alcohol-soluble protein apparently showed uniform physico-chemical properties in both strong and weak flour; the glutenin, however, differed widely from flour to flour in its physico-chemical properties. It appears, therefore, that the question of flour strength is dependent primarily on the physical properties of the glutenin. Viscosity measurements on flour-in-water suspensions brought to a pH of 3.0 by the addition of lactic acid have been found to serve admirably as a means of evaluating gluten quality, and it has been found possible by such measurements to give for the first time a numerical value to gluten quality. Inasmuch as viscosity is such an important property to the emulsoid colloids, it appears probable that the colloidal properties of the gluten gel are the determining factors in flour strength. It is possible to destroy the desirable baking qualities of wheat flours by altering the physical properties of the gluten gel. For example, doughing up a flour with 70 per cent alcohol and immediately evaporating the alcohol at room temperature will ruin a wheat flour for bread-making. On the other hand, such treatment is without effect upon rye flour. Both wheat and rye flour contain the same prolamine gliadin, but rye flour contains no glutenin, and these experiments are regarded as additional evidence that it is the physico-chemical properties of the protein glutenin which cause the variation in the baking qualities of wheat flour. (Variations in baking quality may be caused by factors other than gluten quality. The discussion in this paper is limited to gluten quality and is not intended to include factors influencing yeast activity or variations due to different amounts of gluten.)

Colloid phenomena are likewise concerned in the baking processes and in the baked loaf. During the baking process the proteins are heat-coagulated, causing changes in their water-holding capacity. A part of the starch grains are ruptured, causing the gelatinized starch to absorb moisture, the net result of such changes being that the consistency of the dough is altered to the rather firm texture of the baked loaf. When such a loaf is stored at ordinary temperature it becomes "stale," the stale condition being characterized by a crumbly texture and a feeling of dryness. Apparently, the staling of bread is not due primarily to a loss of water from the loaf, but rather to changes in the protein-starch gel. Several workers have produced evidence that the staling of bread is caused by metastable gelatinized starch reverting to a more insoluble form, with coincident changes in the colloidal properties of the loaf, such as differential syneresis and imbibition in different portions of the loaf.

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[1] Abstract of paper. The complete paper expanded to cover a somewhat broader field will appear as a chapter in a book on colloid chemistry which is to be issued under the editorship of Jerome Alexander.

[2] For a review of the literature dealing with flour strength and the original papers on the relation of flour strength to colloidal properties, see *J. Agr. Research*, **13**, 389 (1918); *J. Phys. Chem.*, **26**, 101 (1922); **27**, 481, 567, 674, 771, in press (1923).

[3] *J. Phys. Chem.*, **27**, 674 (1923).

Panary Fermentation

By C. Brewster Morison

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The process of bread-making may be divided conveniently into three principal stages which are well defined in plant operation. These are, in sequence, the mixing of the raw materials, the fermentation of the resulting dough, and baking. In commercial practice the fermentation period is generally understood to be the total time which has elapsed from the completion of mixing until the dough is ready for scaling or dividing. Actually, however, fermentation changes are initiated during mixing, and continue through the subsequent mechanical operations of making up, receiving an additional impetus from the high temperature of the final rising, or proof, and again at the beginning of baking until further enzymic activities are terminated by the destructive temperature which is reached after a certain period of exposure to the heat of the oven.

The successful control of fermentation, especially in relation to the determination of the time required for the proper development of the dough, so that it can be made up, given the final proof, and baked, is perhaps the outstanding problem of the bread-making process. It involves not only the effective coördination of practically all plant operative conditions from the mixer to the oven, but fundamental considerations relative to the flour, particularly its strength, the properties and composition of the many other ingredients used in bread, and their adjustment or arrangement in formulas. It is thus a problem complicated by a number of variables in any given set of conditions, which include shop operative factors, character of flour and raw materials, and the inherent complexity of the physical and biochemical changes which take place in heterogeneous systems such as a bread dough.

The essential purpose of panary fermentation, expressed in rather general terms, is the effective aeration of dough by the uniform dispersion of a gas throughout the system, which must be occluded and retained by the gluten, so that a well-risen loaf of bread will result on baking, of required volume, grain, texture, taste, flavor, and certain other desirable characteristics. This process must be so conducted that no injury or weakening is done to the colloidal or physical properties of the wheat protein or gluten that determine the capacity for what is commonly termed "gas retention" in the literature of flour strength.

Aeration is primarily accomplished by the use of various leavening agents from biological or chemical sources, of which culture yeast is now the most important. Compressed yeast produced from pure culture strains of the organism physiologically adapted to gas production in the complex environment of dough has practically supplanted the old methods using natural leavens, barms, ferments, and brewer's yeasts, except in certain instances where special types of bread are required; but even here biological culture materials are coming into use, such as the well-known salt-rising ferment of Kohman and the recent "sauerteig" culture of Beccard, for the fermentation of sour rye doughs.

Chemical methods of aeration, such as carbon dioxide under pressure, or a saturated solution of this gas in water, have now little more than historical interest, and chemically reacting compounds which evolve gas in the presence of moisture or heat find their chief application in biscuit and cracker doughs, cake mixes, and self-rising flours. In American bakery practice bread generally refers to the yeast-risen product.

The history of yeast as a leavening agent is of fascinating interest, but cannot be reviewed here. Malouin, who wrote the first book of any value on baking in the eighteenth century, commented enthusiastically upon the introduction of yeast into bread-making, though at that time the varieties used were chiefly impure brewers' yeast. He recognized it at that time as epoch-making in the history of the baker's art. The classical researches of Pasteur, Hansen, and Lindtner, which were to come later, on pure culture yeasts for the fermentation industries have very probably been the most significant scientific influence on the advancement of baking. This statement can readily be appreciated if we imagine what might happen if culture yeast were eliminated from modern commercial practice. Perhaps the future may bring forth synthetic catalysts which will displace yeast. This is obviously a matter of speculation, though of considerable interest to the physical chemist.

The general purpose of panary fermentation has been previously indicated and reference made to the complicated nature of the problem. The remainder of this discussion will be confined to a review of some of the biochemical changes that take place, which appear to be of suggestive interest.

Biochemical Changes

The fermentation of a bread dough is characterized in its general aspects as a complex phenomenon which may be largely attributed to the presence of enzymes associated, not only with the physiological activities of living cells, yeast, and bacteria, but with the flour and other products from biological sources. The typical biochemical changes involved are of the general nature of reactions catalyzed by enzymes, of which the fermentation of hexose sugars by Büchner's zymase, a veritable battery of enzymes, is the most prominent. There appears to be good evidence that the fermentation of sugar by living yeast cells is a typical enzyme reaction. Other changes are the hydrolysis of the disaccharide sugars, sucrose, and maltose, by yeast sucrase and maltase, with the production of the hexose sugars, glucose, and fructose, and that of starch by the diastatic enzymes of wheat flour and other materials such as malt extract, with the production of maltose which may be converted into available glucose.

Some hydrolysis of the protein constituents of doughs, particularly the gluten of wheat flour, probably takes place, though there is little information in the literature regarding it, either as to the extent of such changes, the determining factors involved, or to the sources of the enzymes. This is a problem of immediate interest in connection with fermentation control, particularly in relation to the gas retention properties and coagulation of the gluten, which should include a bacteriological study of the flour and other sources of bacteria.

Effect of Carbohydrates

The carbohydrate materials used in bread formulas, either initially or subsequently available for alcoholic fermentation, are rather extensive. Cane sugar is generally used in most bread formulas in this country, to a greater extent than elsewhere. Other familiar materials are sweetened condensed milk, malt extracts, sirups, and various hydrolyzed products of starch, among which is a dried product of recent interest containing over 90 per cent of reducing sugars as dextrose or glucose.

The amount of sugar initially contributed by the flour is comparatively insignificant. Subsequently, as fermentation proceeds, the amount of sugar available from the flour depends largely either upon its own diastatic power or upon the presence of active diastases from other enzyme-bearing materials such as malt extract. The colloidal condition of the starch is probably of some importance here. The importance of the diastatic content and activity of wheat flour in this connection has been recently pointed out by Rumsey, especially in regard to the importance of sugar production in the later stages of fermentation, particularly in proofing, and during the first few minutes of exposure to the heat of the oven, while the effects of the addition of diastatic products have been investigated by Collatz, who has noted the desirable effects of supplementing the diastatic content in relation to gas production with certain types of flours.

EFFECT OF TEMPERATURE

The influence of temperature on fermentation is well recognized in commercial practice as one of the requirements of successful bread-making.

The temperature coefficient of alcoholic fermentation by living yeast cells has been shown by Slator to be of the same order as for many chemical reactions, though varying considerably, an increase in temperature corresponding with a diminution of the coefficient. Aberson's results, $K_t + 10/K_t = 2.72$, which represents the mean coefficient for 10 degrees between 12° and 33° C., agree well with Slator's observations.

Gas production in the fermentation of doughs, as influenced by temperature under various conditions, has been investigated ever since there was any scientific interest in the subject, and considerable study has also been made of the optimum temperature for various enzymic hydrolyses, especially of the diastases.

In commercial practice straight doughs are usually set at about 26° to 27° C. Dough rooms are maintained at about 27.80° C. The temperature of the proof is considerably higher—32° to 37° C., for example—which greatly increases bacterial, yeast, and enzymic activity. On baking at the usual oven temperature, 230° to 248° C., the center of an 18-ounce dough may reach a temperature of over 63° C. in about 15 minutes. The optimum temperature for diastatic activity appears to be about 63° to 65° C. Collatz has recently found an optimum of 65° C. for malt flour. The presence of bacteria, such as the butyric acid group, which may produce undesirable changes, has received considerable attention in the literature. It does not seem very probable that, with the usual temperature employed and the increased hydrogen-ion concentration which develops during proofing, any appreciably injurious effects will occur from these sources.

EFFECT OF H-ION CONCENTRATION

The influence of the hydrogen-ion concentration on the fermentation of doughs has been a subject of much interest in recent years. This has been due primarily, no doubt, to the more general recognition of the importance of the hydrogen-ion concentration in relation to chemical reactions and biochemical phenomena generally, but more particularly in baking to the inspiration from the well-known investigation of Jessen-Hansen on the baking value of wheat flour. He stated in this paper that "for the dough of any wheat flour, there exists a determined concentration of hydrogen ions with which the bread produced from this flour will be the most successful, and this concentration is greater than that which is found in a dough made from the flour in question freshly milled and prepared with pure distilled water or fresh milk. This optimum concentration corresponds approximately to the exponent of the hydrogen ion pH = 5.0; and that the hydrogen-ion concentration was a little higher for choice flours, and slightly lower for inferior flours, and that the different artificial methods used for increasing the baking qualities of inferior flours are of no value other than increasing the hydrogen-ion concentration of the dough." While the acidity of the dough had long been recognized as of great importance in bread-making, consideration regarding it had been confined before Jessen-Hansen to the gross effects of titrable acidity.

Since 1911, however, the effect of acidity in terms of the hydrogen-ion concentration generally determined by electrometric methods has led to a better understanding of the phenomena involved and the limitations of our present knowledge of its influence on the question of the proper length of the fermentation period with various kinds of flour and other components of bread doughs. Some investigators have apparently considered that, if a bread dough is fermented to about the hydrogen-ion concentration of $10^{-5} N$ or pH = 5.0, the problem is solved, and the time elapsed from the original hydrogen-ion concentration to the development of this optimum is the correct period of fermentation. Unfortunately, however, this does not always follow. Bailey and Sherwood have recently stated, after a long and painstaking investigation in which they followed the changes in hydrogen concentration as pH from the mixing of the dough to the baked bread in a number of large commercial doughs under plant conditions, that they "do not feel that the control of the hydrogen-ion concentration in dough fermentation necessarily implies entire control in practical results."

Their summary of the significance of the hydrogen-ion concentration is of much interest. In their opinion the chief reasons are that the isoelectric point of the gluten is at pH = 5.0, yeast fermentation apparently reaches a maximum at pH = 5.0, flour and malt diastases have their optimum activity, other things being equal, at pH = 5.0, and rope-producing organisms are apparently almost inactivated and their activities reduced in mediums more acid than pH = 5.0. Since patent flour doughs are much less than pH = 5.0, it follows, as far as the foregoing phenomena are concerned, that they all tend to approach an optimum as the dough progressively increases toward pH = 5.0. "Whether some of the phenomena, such as proteolysis, are effected in the same direction has not been determined as yet." Bailey and Sherwood's work emphasizes that, in the estimation of the probable rate of fermentation of bread doughs for their optimum hydrogen-ion concentration, there are a number of variables which must be taken into account, such as grade of the flour, consistency of the dough, temperature, weight of the dough batch, and the influence of materials, the composition and properties of which may influence the rate and direction of the change.

An important point is made in reference to calculating the period of fermentation from initial hydrogen-ion concentration of the dough—that this should be done in relation to the grade of the flour, or that doughs made with lower grades be deliberately acidified at the outset. The addition of acids and acid-reacting or producing materials is of much interest in this connection.

Additions of organic acids such as lactic acid to bread doughs under certain conditions of temperature and proper adjustment of the formula have been found to have a desirable effect in rapidly bringing the dough to the optimum pH for baking.

Another important influence of the optimum hydrogen-ion concentration of bread doughs is in suppressing the activities of certain bacteria other than those of the mesenteric group responsible for rope.

Other Considerations

There are many other aspects of panary fermentation that might be reviewed which are concerned with the effects of various agents, such as free oxygen, electrolytes, fat and other compounds, on yeast and enzyme action, as well as the interrelation of fermentation changes with the physical properties of the gluten for the retention of the gas. The study of lactic acid bacteria suitable for introduction into the dough batch for increasing the hydrogen-ion concentration is now being the subject of considerable investigation. As the tendency in baking has been to shorten the fermentation period ever since it began to adapt itself to large-scale production demands, the future probably will bring forth improvements in this direction both from the mechanical and biochemical sides. The subject in its entirety is such a broad one that many points of interest have necessarily remained unmentioned. If the impression has been created that panary fermentation offers a broad field of study for the chemist and biologist, it will have served its purpose.

The Role of Bread in Nutrition

By Worth Hale

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The importance of an adequate diet in its relation to health and growth of the laboratory animals is clearly understood. So far as animals are concerned, fairly accurate minimum requirements of fat, carbohydrate, amino acids, inorganic substances, and accessory food factors have been established. The adequacy of many individual foodstuffs has been determined and such as have been deficient have been supplemented by the diet as a whole. But among children, where the rate of growth is relatively very slow, the effects of undernourishment are less clearly defined. As a result no one attempts to establish a minimum of the individual food substances required for adequate nutrition, but rather to provide a very considerable excess as a margin for safety. Nevertheless, it is becoming more and more evident that there are many children in this country below the average in weight, height, and health, in some cases because of inherited factors, possibly more often because of faulty hygiene or because of a diet insufficient in amount or in quality. Natural foods are constantly being replaced by prepared foods, either as a matter of choice or as is necessary under conditions involving transportation, preservation, and storage of food in immense quantity. Economic conditions limit the amount and the kind of food. "There are some children the largest item of whose diet is bread. There are numbers of children whose only breakfast is bread and coffee."[1]

The role of bread in nutrition is an important one. During the period 1915 to 1920 the ten-year average per capita wheat consumption for the United States rose from 5.3 to 5.8 bushels.[2] This is nearly 1 pound of wheat per day per person. Some of this represents flour and cereals other than bread, but by far the larger amount is eaten as bread. In England[3] wheat and barley represent 16 million million calories of the total 47 million million consumed. Sherman[4] estimates that in the temperate zone from 40 to 75 per cent of the total calories consumed by the entire population is furnished by cereals and breadstuffs. It is because of this that the nutritive properties of bread should be carefully studied and efforts made to improve its nutritive qualities.

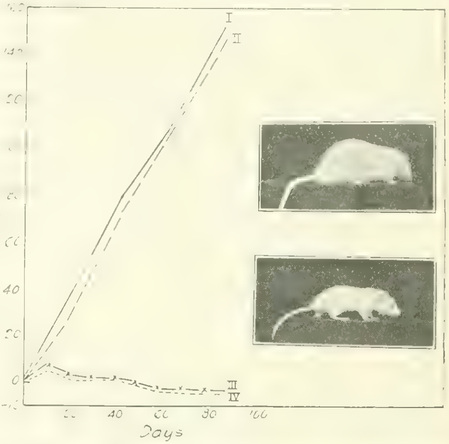

Fig 1—Growth Curve of White Rats Fed upon an Exclusive Diet. I—Normal Laboratory Breeding Diet. II—Special Type Bread. III—Average of Whole Wheat Breads. IV Average of White Breads. Upper Animal Fed on Special Type Bread; Lower Animal on Representative White Bread

Osborne and Mendel[5] have reported that whole wheat serving as 92 per cent of the diet of young rats together with butter fat and salt induced normal growth and reproduction. Sherman, Rouse, Allen, and Woods[6] have shown that a mixture of five parts whole wheat and one part dried whole milk gave a normal rate of growth, reproduction, and the rearing of young. A similar mixture using patent flour was not adequate. However, a bread made with two-thirds white flour and one-third dried whole milk did give apparently normal rates of growth.

As affecting mankind, in Labrador and Newfoundland beriberi, a nutritional disease, was unknown when bread was made from whole wheat flour, but with the introduction of white flour it became a frequent disease. Similar symptoms of undernourishment appeared, on a much larger scale, among the British, who used white bread, but not among the Indian troops whose bread was from coarse whole wheat flour.

One might assume from the foregoing that whole wheat bread should prove far more adequate than white bread. But most so-called whole wheat flour is a degerminated and partly decorticated flour. Flour, whether white or whole wheat, is variously milled and treated, has a protein range from 8 to 20 per cent and the bread into which it is made includes other fats, carbohydrates, proteins, and inorganic salts in varying amounts. If one may judge by the names applied to commercial bread, many contain milk, some, cream, and some, vitamins. Do some of these breads approach in nutritive quality the growth-inducing effects noted by Osborne and Mendel from whole wheat? Are the commercial white breads necessarily so deficient as the experiences in Labrador and at Kut-el-Amara and Sherman's animal experiments suggest?

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[1] Holt, "Food, Health and Disease," **1922**.

[2] World's Almanac.

[3] Sarling, "The Feeding of Nations," p 143.

[4] Sherman, "The Vitamins," **1922**, p. 215.

[5] *J. Biol. Chem.*, **37**, 557 (1919).

[6] *Ibid.*, **46**, 503 (1921).

Bread has been used as the sole diet of a very large series of animals, including mice, rats, and pigeons. In the feeding tests on rodents, groups of from four to ten animals reared from the same stock, which received a diet of 40 parts rolled oats, 24 parts hominy, 16 parts meat scrap, 8 parts dried whole milk, and 1 part table salt, were fed for a period of several months or until the death of the animal. The rate of growth and health of the animals on a bread diet were in all cases controlled by a similar group of animals on the normal laboratory breeding diet. Food and tap water, and in some cases distilled water, were given in sufficient amounts to keep the animals constantly supplied with food. Unless otherwise specified, the rats and mice were young animals, the rats approximating 50 grams, the mice 15 grams. Separate records of each individual were kept, which noted, in particular, changes in weight and in the general condition of the animal.

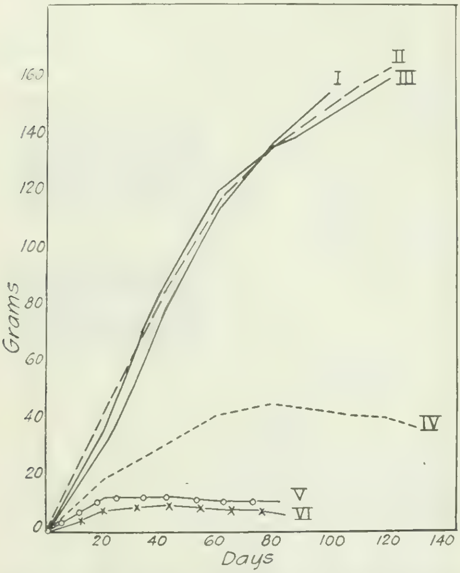

Fig. 2—Growth Curve of White Rats: I—After Donaldson's Normal Curve. II—Special Type Bread. III—Laboratory Normal Diet. IV—Whole Wheat Milk Bread. V—Best Commercial "Whole Wheat." VI—Best Commercial White Bread

Experiments on White and Whole Wheat Bread

In some preliminary tests of commercial bread, two whole wheat and two white breads were selected. These were commercial breads, but one of the whole wheat and one of the white breads contained calcium as a direct addition product (as an aid to the fermentation by yeast). The other whole-wheat bread was labeled to suggest the presence of vitamins. Both whole wheat breads (very probably made in 1918—of war-time flour) were far superior to the two white breads, and one of these, containing added calcium, induced a fair rate of increase in weight of 10 grams at the tenth week, which weight was maintained for 22 weeks, when the experiment was discontinued. During this period two litters of young were born though not reared. The other whole wheat bread, the trade name of which suggested the presence of vitamins, gave not quite so good initial growth, later losses in weight, four of the ten animals died, and no young were born. The two white breads both gave some increase in weight, but later rapid declines with eleven deaths among twenty animals in spite of addition of yeast to the diet, on the seventy-ninth day.

In a later series groups of both mice and rats were fed, using, in addition to the normal laboratory diet, three white and three whole wheat breads. At the end of the experimental period of 3 months the mice on the normal diet had gained more than had any of the other groups fed on bread. However, the mice on one of the white breads (an experimental bread made with milk and an aqueous extract of wheat embryo) had made closely comparable gains in weight. In both groups all animals were in excellent condition during the whole period. The other breads (three whole wheat and two white breads) may be grouped together as not being favorable to growth. A summary of the results appears in Table I.

Table I—Weight Changes of Mice at 13th Week or at Death of Animal

Diet	Gains in Weight Grams				Deaths before 13th Week
Normal diet	13.0	12.4	11.6	9.9	None
Experimental	12.2	10.3	10.1	9.6	None
White	11.2	6.5	5.0	2 9	One
	2.9	2.5	1.1	0.1	Two
Whole wheat	5.4	5.3	4.8	(0.2)	None
	3.8	2.8	1.5	(0.5)	Two
	1.1	0.8	0.4	0.3	All died

Numbers in parenthesis indicate loss in weight.

More striking than these results on mice were those obtained using rats as the test animals. In all cases there is a fair gain in weight during the first week or two, but after that only the control group and the group on the experimental bread continued to increase in weight. The five commercial breads were inadequate to a surprising degree. The results may be summarized as follows:

Table II—Weight Changes of Rats at 13th Week or at Death of Animal

Diet	Gains in Weight Grams				Deaths before 13th Week
Normal	121	121	108	98	None
Experimental	110	86	64	56	
White	42	14	12	10	
	38	18	8	4	One death
Whole wheat	19	14	(2)	(7)	All died
	1	0	(10)	(14)	
	4	(2)	(2)	(4)	

Numbers in parenthesis indicate loss in weight.

As in the case of the mice, evidences of poor nutrition, as indicated by failure to gain in weight, are accompanied by an increase in the number of deaths. The rats, however, seemed to suffer the most, but this may be due to the relative maturity of a mouse at 15 grams as compared with a rat at 50 grams, the initial weights. Younger animals always show a marked unfavorable response to an inadequate diet; older animals show a less striking response, but at times show loss in weight or at most a slow rate of increase. In addition to their failure to induce growth, xerophthalmia, which is associated with a deficiency in fat-soluble vitamin A, was noted among several of the rats on the two whole wheat breads.

In the earlier series the whole wheat breads were noted to be superior to both the white breads in the growth and health of mice, but in this series the experimental white bread was far superior while two commercial white breads (one a so-called cream bread), although much less adequate, were likewise better diets than the three whole wheat breads.

Having secured so much better nutrition from the experimental bread than from the commercial breads, a third series of feeding was begun. Three experimental white breads were made with somewhat differing formula. One contained 4 per cent dried whole milk powder and an aqueous extract of wheat embryo; one, these ingredients and an increase in the protein content by adding 3 per cent peanut protein; the third was made with 6 per cent dried whole milk. Several commercial breads were fed as controls.

Both rats and mice were fed, with results in general agreement with those already noted. The mice were less unfavorably affected by the less adequate bread diets than the rats. The terminal data for the rat feeding covering a 13-week period are given in Table III.

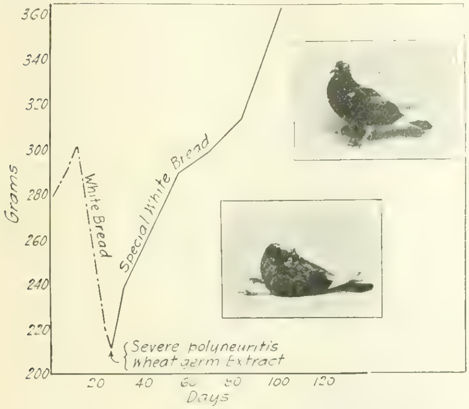

FIG. 3—GROWTH CURVE OF PIGEON ON AN EXCLUSIVE BREAD DIET. LOWER PICTURE—POLYNEURITIS ON REPRESENTATIVE WHITE BREAD. UPPER PICTURE—SAME ANIMAL 5 HOURS LATER—AFTER BEING FED WHEAT GERM EXTRACT

An analysis of the data in Table III shows, as in the second series, that the animals on a normal diet make the best gains in weight. But it is clear with this larger group of experimental and commercial breads that the three experimental breads are distinctly in a class by themselves, providing a diet on which, comparatively speaking, good growth is secured and upon which no animals died. It should be noted that one of the whole wheat breads gives distinctly better growth and maintenance than the others. (Curve V, Fig. 2) The three other whole wheat and the three commercial breads were very deficient from the standpoint of securing adequate nutrition from a single food substance. In another series a whole wheat bread made with some milk gave even better growth (Curve IV, Fig. 2), indicating that milk effectively supplements wheat as an adequate food.

TABLE III—ADDITIONAL EXPERIMENTS ON BOTH RATS AND MICE

Diet		Gain in Weight Grams						Deaths
Normal		161	150	130	101	98	62	One
Experimental	A	103	85	82	80	75	65	None
	Ca	84	59	46	44	..	..	
	B	59	58	56	55	49	47	
White		50	(2)	(2)	(4)	(5)	(7)	Five
		1	(2)	(3)	(4)	(6)	(6)	All died
		1	(3)	(4)	(4)	(5)	(7)	
Whole wheat		16	11	10	10	10	6	Two
		9	8	0	0	(3)	(16)	All died
		4	(1)	(5)	(5)	(8)	(9)	
		1	(1)	(1)	(2)	(6)	(6)	

[a] Only four rats on this bread.
Numbers in parenthesis indicate decrease in weight.

This comparatively good result with the one whole wheat commercial bread may be explained by the fact that it is actually made from whole wheat. The experimental white breads probably owe their better nutritive balance to the added milk and extractive from the wheat embryo. Both are essential, however, for when added to bread separately neither gives a response equal to their combined effect.

EXPERIMENTS WITH SPECIAL TYPE BREAD

One commercial white bread, deserving separate consideration, has been studied to determine its adequacy as a diet. This bread is made with whole milk, extract from wheat embryo, and added calcium. On analysis it shows especially a higher protein content, more fat, particularly butter fat, and a higher ash content than the average white bread. The analysis shows 43.9 per cent starch, 8.9 per cent protein, 5.4 per cent fat, including 1.8 per cent butter fat. The potassium content exceeds that of the average white bread by three times, calcium by ten times, iron by two times, and phosphates by 2.5 times.

Rats have made excellent gains in weight when fed on this white bread, exceeding very materially the growth already noted of those animals upon the several experimental breads. In fact, animals on this bread diet have grown quite as rapidly as normal animals, some showing more rapid, others less rapid growth. So far as can be determined, the differences in the rate of growth are more related to the normal variation in animals from the same stock than to the diets of bread or of the mixed grains, meat, and milk of the control groups.

A summary showing increases in weight of three series, each of 12 weeks' duration, is given in Table IV.

TABLE IV—COMPARISON OF SPECIAL AND NORMAL DIETS

Diet	Gain in Weight Grams				
Normal	140	133	122	101	Series I
Special	138	137	131	128	
Normal	179	169	164	152	Series II
Special	168	157	143	140	
Normal	161	155	154	143	Series III
Special	163	149	144	136	

The twelve rats on normal food gained 1773 grams, those on this bread 1734 grams. The weekly average gain for the rats on normal food was 12.31 grams, or those fed on bread 12.04 grams. These results are distinctly in contrast to all feeding tests made on commercial bread, either white or whole-wheat, and on experimental bread made by the addition of milk (in smaller amounts) and an aqueous extract of wheat embryo.

Fig. 1 illustrates in detail the rate of growth of animals fed upon an exclusive diet of this bread (terminal data in Table IV) and on other breads (terminal data in Tables II and III).

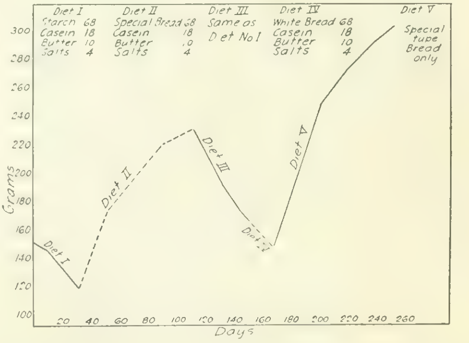

FIG. 4—GROWTH CURVE OF A WHITE RAT ON VARIOUS DIETS. VITAMIN B DEFICIENCY IN WHITE BREAD; ADEQUATE AMOUNTS IN NEW TYPE WHITE BREAD

Fig. 2 is drawn from data obtained in an experiment of longer duration with curves to show Donaldson's normal growth curve, the normal curve of the control animals, of animals fed on this special white bread, on a whole wheat bread made with some milk, and on the best of the commercial whole wheat and white breads.

That this bread owes its superior growth-inducing qualities in part to an adequate amount of vitamin B is shown by feeding pigeons. On ordinary white bread, polyneuritis developed in about 3 weeks. The same pigeon, after having been cured by feeding vitamin B in concentrated form, remained in good health and grew normally for several months, although fed only this white bread. (Fig. 3) Similarly, of two pigeons fed on bread, the pigeon fed one of the average white breads developed polyneuritis on the eighteenth day, and subsequently died. The other has been fed this special white bread for many months with no apparent impairment of growth or health.

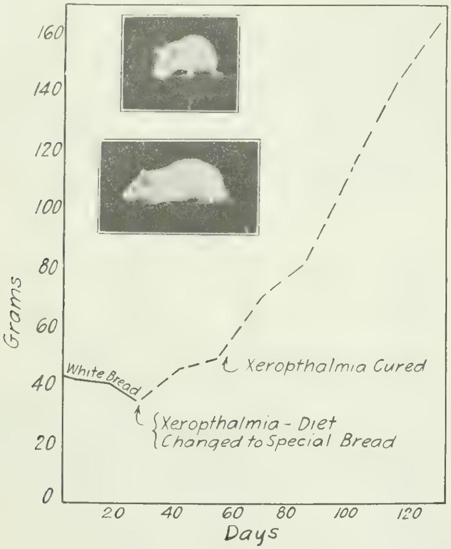

Fig. 5—Growth Curve of a White Rat. Vitamin A Deficiency in Ordinary White Bread; Adequate Amounts in the New Type Bread. Top, Xerophthalmia on White Bread; Bottom, Cured and Normal Growth on New Type Bread

That vitamin B has this pronounced beneficial effect on nutrition from a diet of white bread is further shown by the fact that a diet of purified foodstuffs—starch 68, casein 18, butter fat 10, inorganic salts 4 per cent—leads to rapid loss of weight, as does also this diet mixture in which the starch is replaced by ordinary white bread. This purified diet may, however, be made sufficient for normal growth when 0.3 gram brewers' yeast is added or when the starch is replaced by this new type of bread or when the whole mixed diet is changed to a diet of this bread alone. This is demonstrated in Fig. 4, which shows graphically a part of the life history of an individual rat whose diet was changed from time to time.

The average commercial bread, with fat derived from vegetable sources, is necessarily deficient in vitamin A. This is shown by the development of xerophthalmia. Not only has this not developed when feeding this new white bread, but such bread when given to animals with xerophthalmia cures the disease and induces normal growth, a contrast which is shown graphically in Fig. 5.

The increased inorganic salts may likewise play some part in the superior nutritive property of this new bread. Repeated experiments have shown that bread salts are not physiologically adequate, and that additions, particularly of calcium, to diets increase the growth response, or in the case of isolated tissues (the frog's heart) the activity of the tissue.

As a supplement to the animal tests, the coöperation of a small institution housing children was secured. The diet in this home is rather ample and of considerable variety, so that no large changes were expected by changing the bread used. The children in the home were divided into two groups according to age and sex. To one the regular institutional diet was given, which fortunately included one of the white breads already studied on animals. The other group received the new type of bread, but in no other respect was there any change made or suggested in the diet. Of the forty-five children, thirty remained in the home several months. Measurements without clothing were made every 2 weeks. The test was discontinued at the end of 9 months. The eight boys on the ordinary white bread gained 4.26 pounds more than the expected gain at their age, averaging 0.53 pound more for each child. The similar group of seven boys on the special bread gained 6.33 pounds more than was to be expected during the same period and age—an average gain over the expected rate of 0.90 pound for each child.

The girls in both groups made larger gains than the boys, which suggests that the total calorie intake was low and affected the more active boys to a greater degree. Of the group of seven girls on ordinary white bread each gained 2.28 pounds more than the expected average, while of the group of eight girls on the special bread each averaged 2.46 pounds greater gain, and this in spite of the fact that one of these girls, mentally backward and losing weight, is included in the latter group. To exclude this individual the gains would be 2.28 in one case and 3.28 in the other. The numbers are too small for one to venture conclusions, but the fact remains that, in spite of small numbers and with only about 700 calories of the total diet changed, the special bread groups consistently made better weight increases.

This new type of white bread clearly stands in a class by itself. Not one of the other breads begins to compare with it as a well-balanced food. Much of that which wheat had lost in the milling and refining process has been returned to the bread in concentrated form. The proteins of the wheat have been supplemented and made adequate by the addition of a natural food product, milk. It is significant that the full nutritive value of bread, the fundamental criterion of excellence of bread, is being developed in that industry which supplies nearly one-third the calories in one's daily food!

Symposium on Heat Transfer

As previously announced, a Symposium on Heat Transfer will be held at the spring meeting of the American Chemical Society, under the auspices of the Division of Industrial and Engineering Chemistry. A number of papers are in preparation by writers well versed in various applications of heat transference. These papers may be classified as follows:

1—Heat Losses by Radiation plus Convection, through Bare and Insulated Surfaces
  (a) From Pipes (b) From Furnace Walls
  (c) From Miscellaneous Shapes
2—Heating or Cooling of Noncondensable Gases
  (a) The Warming of Air in Hot-Blast Heaters
3—Heating or Cooling of Liquids Flowing inside Pipes
  (a) Water (b) Oils
4—Condensation
  (a) In Surface Condensers and Water Heaters
5—Evaporation
  (a) The Analysis of Certain Comparative Tests on Evaporators
  (b) Heat Transfer in Enameled Apparatus
6—Miscellaneous Topics
  (a) "A Heat Meter"
  (b) The Determination of Air in Steam, and the Importance of This Factor in Heat Transmission

In order that those interested may have ample time to prepare discussion of these papers, advance copies bound under one cover will probably be issued. To this end it is necessary that the complete manuscript be in the hands of the chairman, W. H. McAdams, Massachusetts Institute of Technology, Cambridge, Mass., not later than January 15, 1924.

Erle M. Billings, *Secretary*

Reproduction of Animals on an Exclusive Diet of Bread[1]

By Charles Hoffman

Ward Baking Co., New York, N. Y.

The problem of building a loaf of bread—one that is white of crumb and one with the degree of lightness demanded by the American public—was more than merely adding the vitamin B and vitamin A factors. It was necessary to balance the proteins and the mineral salts in order to obtain a product which would be of real benefit to humanity. The problem was difficult; at every step fermentation and baking problems were encountered. The question of producing lightness in a loaf which contained such a large quantity of wheat extract was a problem to solve, and when the protein was increased the leavening problem became doubly difficult. Then the keeping and eating qualities of the loaf had to be considered. There was no idea of commercializing the discovery of the vitamins. The aim was to produce in bread a well-balanced food. Bread is the chief food of all civilized nations, is eaten at every meal, and totals from 20 to 70 per cent of the daily food consumed.

The chief questions which we need to consider in regard to a super-bread of this type are—does it bring economy to the consumer, and is it needed in the American diet? The consumer is entitled to know whether it is economy to pay 3 to 4 cents more per 22 ounces of bread for a super-bread than for common bread. As a matter of fact, it is economy. In the first place, the same nutritive value could not be obtained through eggs, milk, cereals, meat, potatoes, and vegetables at twice the cost that can be purchased through the super-bread. The loaf of bread is an economical medium for delivering rich whole milk to the consumer. Whole milk can be delivered at 9 cents a quart in a loaf of bread. The milk in this form is safe for children, and when baked in combination with the other dough ingredients makes a food which can be digested and assimilated by the weakest stomach.

The results of diet studies and observations among school children show the need of a super-bread in the diet. The selective draft during the last war found 30 per cent of America's young men to be physically unfit for military service. Authorities state that the visible malnutrition and undernourishment among our school children runs much higher than 30 per cent. There are, no doubt, an equal number which are undernourished but show no visible defects. Improper selection, economy, transportation, and distribution of food are the chief contributing factors causing malnutrition. This seems strange because this nation has an abundance of food, and food of the right kind. The right kind of food, however, is not selected by the consumer so as to produce a balanced diet. Still there is the important fact that the great majority of the public does not understand the newer principles of nutrition. The results of an improper diet are not confined to children; a large percentage of grown-ups show defects from improper diet. Lowered resistance and easy fatigue, indigestion, and intestinal disorders are a few of the results of poorly balanced diets.

Dr. McCarrison, of the Royal College of Physicians and Surgeons of England, has made an extensive study of the diets of men and women in England and compared these with the diets of men and wild animals in Asia. In his lecture at the University of Pittsburgh in January, 1922, Dr. McCarrison stated that much of the gastro-intestinal disorder of civilized people at the present day is due to faulty diets. He found, during his nine years of professional work in the remote part of the Himalayas far removed from the refinements of civilization, that certain races are of magnificent physique, preserving until late the character of youth; they are usually fertile, long-lived, and endowed with nervous systems of notable stability. During his stay among these people he never saw a case of authenic dyspepsia, of gastric or duodenal ulcer, of appendicitis, of colitis, or of cancer, although he averaged four hundred major operations per year. He found their buoyant health a notable contrast with the dyspeptic and colonic afflictions which he encountered among the highly civilized communities upon his return to the West. The people in these communities live upon unsophisticated foods of nature—milk, eggs, grains, fruit, and vegetables. Dr. McCarrison concluded that the enforced restriction to the natural foodstuffs of nature was compatable with fertility, long life, continued vigor, perfect physique, and a remarkable freedom from digestive and gastro-intestinal disorders and from cancer. McCarrison agrees with Hindhede, who affirms on unequivocal evidence that the two chief causes of disease and death are food and drink.

Drs. Packer and Moehlen, in examining 84,389 children for height, weight, size, and school standing, found with but few exceptions that at every age from 6 to 14 years the degree of backwardness or progress in school work follows closely the undernourished or well-nourished condition of the child, as measured by height and weight.

In this country we are rarely confronted with a serious deficiency of any one food factor in the diet. We are confronted, however, with the problem of obtaining the proper amounts of all the factors. The most dangerous condition exists where we are just below the subminimal amount of any one factor. Under these conditions defects in the diet are seldom observed and may not be evident until late in life and through succeeding generations. Where subnormal conditions are observed they may be ascribed to other causes than the diet. The tendency is to look for an actively injurious substance rather than the absence of one or more essential nutritious elements.

McCollum[2] states:

> The evidence is overwhelming that the keynote of successful nutrition is the selection of foods having unlike dietary properties, but so constituted as to supplement each other's deficiencies and to make a mixture which affords the most satisfactory amounts of each of the essential food elements, rightly combined. The generalization has been made that a diet may afford a surprisingly great variety of foodstuffs, including cereal grains, tubers, fleshy roots, fruits, and liberal additions of muscle meats, and still fall far short of being adequate for the support of growth or for the maintenance of health in the adult.
>
> The diet must be considered as a whole, and an accurate estimate made as to the degree of completeness of every essential factor. Since in this country the term "high protein diet" is generally synonymous with "high meat diet," it will be seen that disturbances of nutrition believed to be referable to excessive protein ingestion may well be due, not so much to the amount of protein eaten, but to failure to take a complete diet. Such a diet is only to be secured through the proper selection of foods which make good each other's deficiencies. It is the completeness of the diet rather than an unusual amount of some one factor which is the most important consideration.

The effect of a partial deficiency in the diet is best illustrated in Chapter XI of "Vitamins and the Choice of Foods," by C. C. and R. H. A. Plimmer. This shows what the effect of border line nutrition means to the health and vitality of the individual. By making bread rich in vitamins, proteins, and mineral salts, a factor of safety is introduced at every meal which guards against any deficiency in the diet and which will raise many of the diets on the border line of nutrition to a point where all the necessary elements are provided for best growth and health. The following is taken from this chapter:

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[1] Discussion of preceding paper by Worth Hale on "The Role of Bread n Nutrition."

[2] "The Newer Knowledge of Nutrition."

Between the complete absence of any one vitamin, causing beriberi, scurvy, etc., and a diet containing a sufficient quantity of all the vitamins, numerous variations are possible, and many people exist upon a diet between these two extremes. The value of a diet cannot be judged by its palatability and apparent variety. The unpalatable and monotonous diet adopted in Denmark during the war is in striking contrast to a common diet of the poorer classes in this country, as shown below.

The Danish diet contained all the vitamins, and good protein was provided by the milk; meat was practically unobtainable except by the very wealthy. During the period of its consumption the death rate fell by 34 per cent, thus demonstrating its efficiency. From this experience Hindhede, a Danish physiologist, concluded that "the principal cause of death lies in food and drink."

Danish War Diet	British Working-Class Diet
Bread made of whole rye + wheat bran + 24 per cent of barley	Bread, cakes, and puddings made from white wheat flour and other prepared cereals
Barley porridge	Oatmeal porridge
Potatoes	Potatoes
Greens	Meat and vegetable stew
Milk in considerable quantities	Margarine
Butter	Corned beef, tinned salmon, etc.
	Bacon
	Kippers, bloaters, smoked haddock
	Cheese
	Milk in small amounts
	Jam, pickles, sugar, sirup, tea, coffee, cocoa
	Sago, tapioca, pea flour, etc.

The nature of the deficiency in the British working-class diet is not the complete absence of any one vitamin but a shortage of all of them; neither *A*, *B*, nor *C* factor is present in abundance and may be further reduced by methods of cooking. The diet contains few natural foodstuffs which have not been prepared or preserved in some way. The occasional addition of eggs, fruit, and real butter, the daily use of potatoes and of small quantities of milk avert rapid disaster, but the diet is not consistent with good growth in children nor with good health in persons of any age.

The Danish war diet consisted entirely of natural foodstuffs. McCarrison refers to another example of a monotonous diet which is good because it contains only natural foods. The people of the State of Hunza, in the extreme north of India, live solely on wheat, barley, maize, fruits, especially apricots, goats' milk and butter; goats' flesh is only eaten on feast days. The people are unsurpassed in perfection of physique and freedom from disease in spite of the hard climate and lack of sanitation; appendicitis is unknown; they have an extraordinarily long span of life.

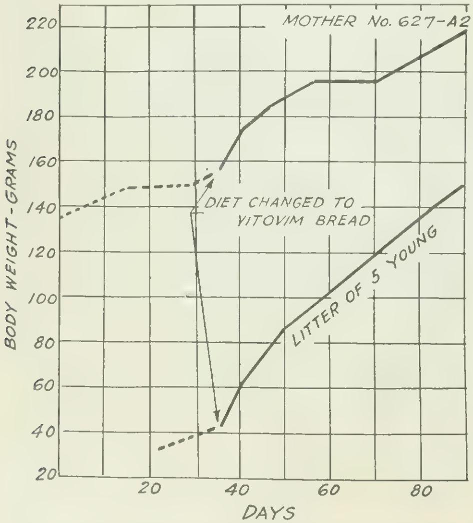

Chart 1—Curves Showing How a Diet Ordinarily Complete for an Adult Mother Is Deficient for the Same Mother While Nursing a Litter of Young. When the Diet Is Changed to Vitovim Bread Both Mother and Young Make Normal Growths

During the last decade research on the various factors, proteins, mineral salts, and vitamins has shown the importance of their relationship to growth and the maintenance of health in test animals. The study is now being carried further. The effect that these various factors have upon reproduction is being noted. It has already been shown that a diet adequate for producing normal growth in young and for the maintenance of weight is not adequate for normal reproduction. A diet may be adequate for reproduction but not for the rearing of the young; or it may be adequate for rearing young but not for raising successive generations. The amounts and quality of the proteins, the amount of the vitamins, and the mineral salts must be increased in the diet in order that normal reproduction can be carried into successive generations. All these studies have been greatly simplified since the discovery of the vitamins, and with it the establishment of standard diets in which all the food factors, so far as we know, are known and can be controlled. After the standard diet consisting of purified substances was shown to be adequate for growth and reproduction, it was natural that the investigators turned to food products to study the completeness or the inadequacy of the individual foodstuffs. In making these tests the food under consideration is the principal component of the diet. Additions are then made of one or more purified food substances (varying the amounts), like protein, mineral salts, and the individual vitamins. The animals on the diets containing these factors are then watched for growth and reproduction.

Effect of Different Food Factors upon Reproduction

The history of these early experiments is well known, so it is needless to repeat them here. A brief review, however, of the effect of these various food factors upon reproduction will be given because of their relationship to the development of a well-balanced nutritious loaf of bread which is adequate for normal growth and adequate for successive reproduction through numerous generations.

McCollum and Davis[3] point out the importance of carrying on reproduction into successive generations upon a diet before it can be considered adequate. They state:

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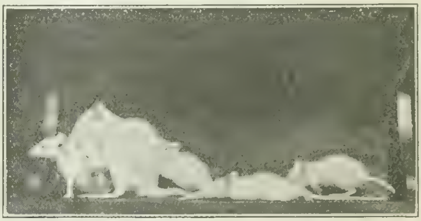
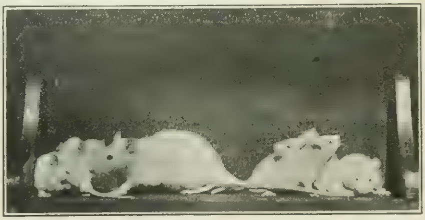
[3] *J. Biol. Chem.*, **21**, 615 (1915).



Animals Previous to Change in Diet



Same Animals after 2 Weeks on Vitovim Bread

Growth to the normal adult size at the usual rate and continued well-nourished appearance is not sufficient evidence that a ration is fully adequate. Only when normal reproduction and rearing of the young is repeated at normal intervals can a ration be said to be physiologically sufficient.

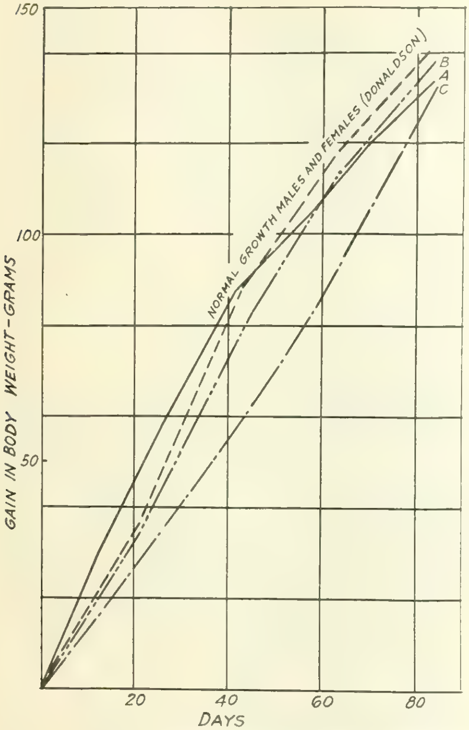


Chart 2 —Comparative Growth on Vitovim Bread Obtained at the Following Laboratories:

A—Ward Laboratory, N. Y. City. 4 Rats, 2 M–2 F. Weight at start, 48 grams

B—Mellon Institute of Industrial Research. 9 Rats, 6 M.–3 F. Weight at start, 55 grams

C—Biological Laboratory, Eastern University. 4 Rats, 2 M.–2 F. Weight at start, 48 grams

McCollum has shown that a diet consisting of:

	Per cent
Whole wheat	67.5
Casein	15.0
Whole milk powder	10.0
Sodium chloride	1.0
Calcium carbonate	1.5
Butter fat	5.0

is adequate for normal growth and normal reproduction.

Evans and Bishop,[4] by studying the oestrous cycle of the rat, have shown that this diet contains all the elements necessary for the normal reproductive function in the rat. It is adequate in protein, both as to amount and quality, proper mineral salts, and vitamins A and B (and possibly enough vitamin C) for optimum growth and reproduction with the albino rat.

The work of Sherman, Osborne and Mendel, McCollum, Steenbock, Evans and Bishop, and others has shown that the amount of these food factors necessary for growth and maintenance of vigor is less than that required for normal reproduction and healthy rearing of young. A diet may thus be adequate for producing normal growth but still be inadequate for reproduction.

It would be an error to conclude that any one factor would be the predominating one that effects reproduction. There is sufficient evidence to show that a diet which is below the optimum in any nutritive factor will seriously affect the reproductive function in the rat. There is also plenty of evidence to show that lack of vitamin B atrophies the reproductive organs, that lack of vitamin A effects the oestrous cycle of the rat long before any other physical defects are visible, that lack of the proper amount of the proper quality of protein prevents normal rearing of young and that lack of proper mineral salts vitally affects the nursing young.

Vitamin B Deficiency—McCarrison[5] observed marked atrophy of the testes of males and the ovaries of females due to this deficiency.

Drummond[6] found sterility among animals on a diet deficient in vitamin B and that a diet containing an abundance of this factor was favorable to reproduction.

Sherman[7] states: "Successful reproduction and lactation may demand a higher concentration of vitamin B in the diet than is needed for the maintenance of health or even for the support of normal growth."

Evans and Bishop[4] noted complete cessation of ovulation with the rat. The ovarian function ceased entirely when vitamin B was lacking in the diet.

Vitamin A—Drummond finds that a liberal allowance of vitamin A in the diet produces better reproduction.

Sherman and MacLeod[7] show that diets ample in vitamin A for growth and health may show a most marked influence upon the capacity to produce and rear young.

McCollum and Steenbock have also shown that diets which are adequate in vitamin A for growth are not adequate for reproduction, and diets adequate for reproduction are not necessarily adequate for rearing of the young.

Reynolds and Macomber[8] have found a decrease in fertility to result from a lack of vitamin A in the diet.

Davis and Outhouse[9] experimenting with a diet of crushed oats, polished rice, and skimmed milk, *ad lib.*, and a limited

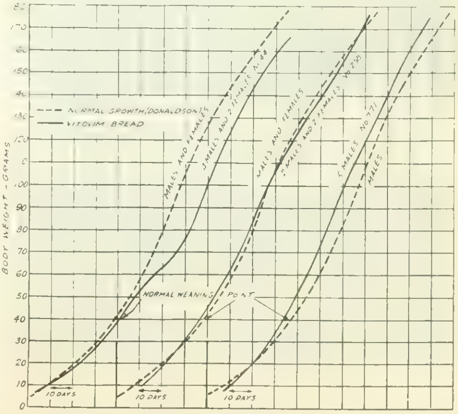


Chart 3—Growth Curves Showing That Young Born and Raised on Vitovim Bread Grow Normally Both before and after the Weaning Period

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[4] *Metabolic Research*, **1**, 335 (1922).

[5] *Indian J. Med. Research*, **6**, 275, 550 (1917).

[6] *Biochem. J.*, **12**, 25 (1918).

[7] "The Vitamins," **1922**.

[8] *J. Am. Med. Assoc.*, **77**, 169 (1921).

[9] *Am. J. Diseases Children*, **21**, 307 (1921).

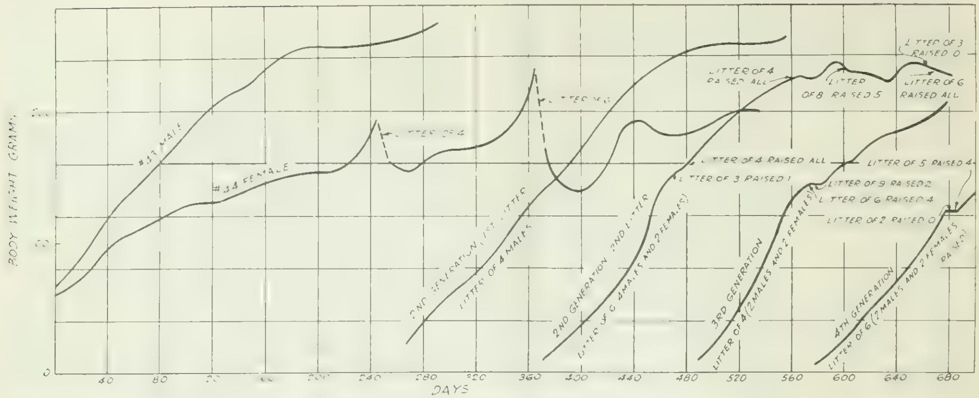


CHART 4—REPRODUCTION ON VITOVIM BREAD

amount of cooked potato and egg white, found that the males lived no longer than 8 months. Most of the females reared one litter and a few two litters. Of the twenty-three females born, seven produced litters and only two of these litters were reared. Xerophthalmia appeared at 4 to 5 months on this ration. The second generation showed marked anemia and the bones were very fragile. This clearly demonstrates the effect on reproduction when the diet contains only a limited amount of vitamin A.

Evans and Bishop, following the method developed by Evans and co-workers in the Department of Anatomy of the University of California, have made significant observations upon the relationship of vitamin A to reproduction. They find a prolongation of the oestrous cycle and failure of ovulation in 100 per cent of the animals which are reared on diets low in vitamin A but which nevertheless have permitted preliminary normal growth.

Female No. 258 with Her Litter of Nine—Mother Having Been Raised on Vitovim Bread

The Same Litter 6 Weeks Later—Mother Was Able Successfully to Nurse and Raise Her Entire Litter on Vitovim Bread and Water as Her Exclusive Diet

PLATE I

They further state: "The disturbance of oestrus from fat-soluble vitamin A deficiency is highly characteristic, resembling no other nutritive upset known to us."

Usually when the test is given, other signs of vitamin A deficiency, such as weight decline, have appeared, but this characteristic continuance of the oestrous smear may precede all other signs of vitamin A, and, furthermore, is shown in conditions where vitamin A is not so low as to cause growth, failure, or xerophthalmia. It may thus constitute the only sign of vitamin lack save failure to reproduce successfully.

PROTEIN AND MINERAL SALTS—Using their method they found, as before stated, that when vitamin B is lacking in the diet there is complete cessation of ovulation. Their experiments further show that a diet of McCollum's consisting of:

	Per cent
Wheat	60.0
Sodium chloride	1.0
Calcium carbonate	1.5
Dextrin	32.5
Butter fat	5.0

will maintain adult animals for 100 to 200 days without apparent injury; the young, however, are badly stunted if reared upon it. They find the young behave in their sexual physiology similar to "runts" created by quantitative undernutrition. The oestrous periods were entirely absent with seven of the thirteen animals, and only three of the other six exhibited other ovulations. By the addition of casein to the diet they were able to effect a restoration of the normal cycle.

McCollum and co-workers state that the mother rat destroys the young soon after birth when the diet is low in protein. This they found to be the rule among animals which were restricted to diets inadequate in protein and when the protein was of poor quality.

Evans and Bishop find that animals restricted to a diet poor in mineral salts exhibited abnormal oestrous phenomena, although the growth of the animals manifests no ill effects on this diet. They stated that salt depletion is not only inimical to skeletal growth but also to the normal rhythm of ovulation.

McCollum observed that young rats which were nursed by mothers whose diets were deficient in mineral salts, notably calcium, developed typical symptoms of tetany. The young would appear to be well nourished for the first two weeks of nursing, then would suddenly develop paralysis.

Observations on Single Food Products—Hart and Steenbock[10] showed that for long, vigorous maintenance and reproduction the seed and seed products are deficient, even if common salt and natural water of relatively high calcium content are supplemented. They carried out their experiments with swine and observed that maintenance could be secured with grains and grain products for a considerable length of time but complete nutrition and reproduction were impossible on such a diet.

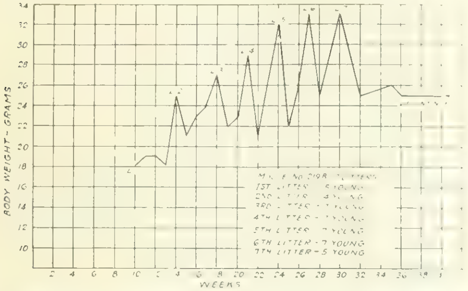
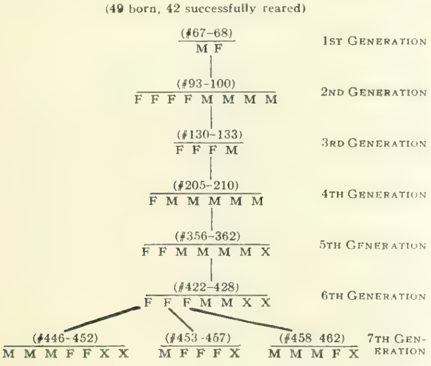


Chart 5—Regular Reproduction on a Diet of Vitovim Bread and Water. The Female Was of the Second Generation Born and Raised on the Bread. This Mouse, in Spite of the Repeated Reproduction, Made a Consistent Gain in Weight

Slonaker and Card[11] studied the effect of a restricted diet (a diet corresponding fairly closely with the so-called vegetarian diet of human beings) upon a number of litters and young born. They found that animals whose diet was restricted to plant sources lost the power of reproduction by the third generation and the line of descent became extinct.



(X denotes young that died)

Chart 6—Seven Generations Raised on Vitovim Bread as Sole Food

It is now well known that any one seed or grain or combination of seeds and grains does not support normal growth, all of them are lacking in the proper kind of protein, lacking in sufficient lime salts, and most are lacking in vitamin A. Under these conditions we would expect no normal reproduction from animals receiving nothing but seeds or grain in their diet.

McCollum, Simmonds, and Pitz[12] found that the oat kernel supplemented by protein, salt mixture, and butter fat gave about normal growth but reproduction was a complete failure. The failure in this case is due to a poorly balanced protein, as in this paper it was shown that casein did not supplement the protein of the oat kernel.

Experimenting with wheat as the sole source of protein, the same writers[13] could not make up a ration which was adequate for rearing of young, although they varied the protein content from 6.5 to 47.98 per cent. Over a wide range of protein content growth approximated the normal, but pronounced injurious effects of the ration were revealed only in the reproduction records.

They further showed that 15 per cent of whole wheat as the source of vitamin B was sufficient for completion of growth and normal production of young. The amount of the vitamin B present, however, was not great enough to enable the young to develop to weaning age without causing pronounced nervous disturbances which ended in death.

McCollum[14] reported growth approximating the normal rate and successful reproduction in rats fed exclusively on boiled egg yolk. This ration contained about 31 per cent of protein ($N \times 6.25$). He further found that, in spite of the fact that egg yolk contains all the organic complexes essential for nutrition, it does not form a satisfactory ration when gaged by the amount of reproduction secured or by the longevity of the animals so fed.

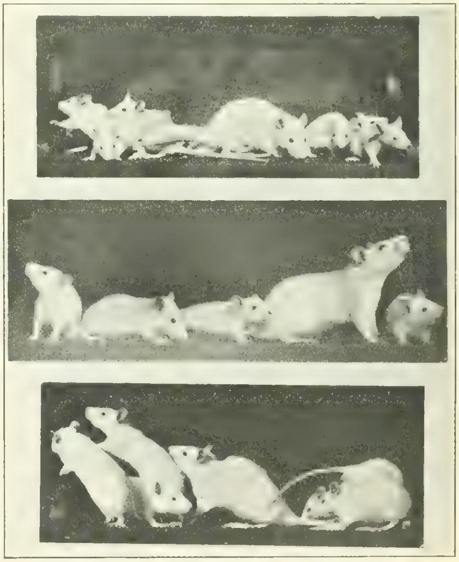


Plate II—Typical Mothers and Their Litters of Young Raised on an Exclusive Diet of Vitovim Bread and Water

Sherman and co-workers[15] showed that a diet consisting of 5 parts of ground whole wheat and 1 part of whole milk powder supported normal growth with successful reproduction and rearing of young. However, when the whole wheat was replaced by patent flour the ration was not adequate for normal reproduction and successful suckling of the young. They obtained an interesting result on feeding a female, which had been seriously stunted in early life by feeding upon bread alone, equal weights of bread and market milk. The animal resumed growth at a normal rate, and when fed a mixture consisting of 1 part whole milk powder and 2 parts of ground whole wheat was able to produce healthy young and suckle them successfully so that they grew at a normal rate and one of them at an early age produced vigorous young of the third generation.

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[10] *J. Biol. Chem.*, **39**, 209 (1911).

[11] *Am. J. Physiol.*, **64**, 167 (1923).

[12] *J. Biol. Chem.*, **29**, 341 (1917).

[13] *J. Biol. Chem.*, **28**, 211 (1916).

[14] *Am. J. Physiol.*, **25**, 120 (1909).

[15] *J. Biol. Chem.*, **46**, 503 (1921).

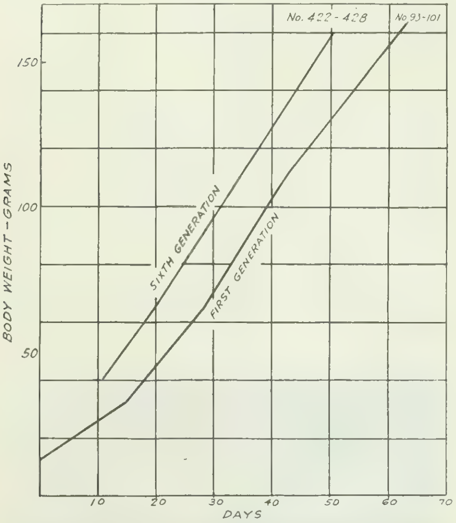

Chart 7—Normal Growth Obtained in First and Sixth Generations of Mice Fed Exclusively on Vitovim Bread and Water

Their results further showed that on a diet consisting of bread and milk (five-sixths bread solids and one-sixth milk solids) very few young could be reared, though reproduction was almost normal. In fact, only one of the many females which they raised from the weaning age on the ration of bread and milk succeeded in raising her young.

Mattill and Conklin[16] were unable to get normal reproduction from animals reared on fresh or powdered milk. When they added 5 per cent of yeast and 2 per cent of a salt mixture they obtained animals of the fourth generation.

Evans and Bishop[17] describe an unidentified food factor, *X*, which they claim is a dietary essential necessary for reproduction. Using the following diet:

	Parts
Casein	18
Corn starch	54
Lard	15
Butter fat	9
Salts	4
Dried yeast	0.4 gram per day

they find their rats to be sterile, and ascribe it to the lack of a food factor, *X*. Fertility is restored to the animals on the foregoing diet by the use of green leaves or dried alfalfa leaves or when butter fat is increased to 24 per cent. Evans and Bishop state that cod-liver oil is lower in this *X* factor than butter fat. They find *X* to be present in whole wheat, but lacking in orange juice. Wheat germ is rich in this factor. They further state that yeast apparently contains a substance toxic to the reproductive organs.

Nelson, Heller, and Fuhner[18] conclude that "the postulation of a new vitamin for reproduction is unnecessary. Third generation animals have been reared on 5 per cent of yeast as the sole source of vitamin B in the diet. They also found that the majority of young are not reared on synthetic diets containing yeast as the only source of vitamin B."

The Ward Laboratory found:

	Parts
Casein	18
Starch	68
Organic and mineral salts[a]	4
Butter fat	10
Yeast	5

[a] Osborne & Mendel Salt Mixture.

to be adequate for reproduction into the second generation. Either the butter that was used contained a liberal amount of the factor *X*, which Evans and Bishop think is necessary for reproduction, or else the yeast carried an abundance of that factor. They think the diet used by Evans and Bishop was deficient in vitamin B.

A peculiar incident happened while feeding this diet. The young of the second generation while they were still nursing seemed to be abnormal. They ran about in circles in their cages and remained on their feet with difficulty—in fact, some showed signs of paralysis. It was discovered that the failure to support the young on this diet was due to a lack of vitamin B. The yeast had lost its potency in the vitamin B factor during storage. Some of the mothers with their litters

Comparative Analysis of Breads

	Vitovim Bread	Average Good White Bread	100% Whole Wheat Bread
Grams per Pound of Bread (28.3 grams = 1 ounce)			
Moisture	172.1	172.1	172.1
Starch	199.3	213.4	187.4
Protein ($N \times 5.7$)	40.5	33.7	39.1
Total fat	16.3	10.4	17.2
Butter fat	8.2	1.3	2.0
Ash	9.6	6.5	11.0
Sugar	15.0	16.6	17.4
Lactose	10.2	1.6	2.0
Fiber	0.4	0.3	9.0
Grams Mineral Matter per Pound of Bread			
Chlorine	2.90	3.08	3.04
Phosphates	2.37	0.86	3.13
Potash	1.54	0.50	1.54
Sodium	1.81	1.77	1.95
Sulfates	1.13	0.45	0.95
Magnesia	0.23	0.20	0.77
Lime	1.76	0.15	0.31
Silica	0.050	0.059	0.045
Iron	0.021	0.010	0.024
Manganese	Trace	...	Trace
Bromine	Trace	Trace	Trace
Analyses in Detail—Per cent			
Moisture	38.00	38.00	38.00
Starch	43.98	47.10	41.36
Protein ($N \times 5.7$)	8.94	7.44	8.52
Total fat	3.60	2.29	3.78
Butter fat	1.80	0.28	0.45
Ash	2.11	1.43	2.42
Lactose	2.26	0.35	0.44
Total sugar	3.28	3.67	3.84
Crude fiber	0.09	0.07	1.98
Mineral Content of Breads—Per cent			
Chlorine	0.64	0.68	0.67
Phosphates	0.50	0.19	0.69
Potash	0.34	0.11	0.34
Sodium	0.40	0.39	0.43
Sulfates	0.25	0.10	0.21
Magnesia	0.05	0.045	0.17
Lime	0.39	0.032	0.068
Silica	0.011	0.013	0.010
Iron	0.0045	0.0022	0.0052
Manganese	Trace	...	Trace
Bromine	Trace	Trace	Trace

Three mothers with their litters of young, while still nursing were placed on Vitovim bread, 100 per cent whole wheat bread, and an ordinary good white bread, as their sole diet. The litter on the super-bread, made notable gains from the start, while on the whole wheat bread diet death occurred with all the young in less than 1 week's time. The young became completely paralyzed before death occurred. On the white bread the young lived a short time but none of them made any gain in weight. The young on the super-bread made an average gain of 120 grams in as many days.

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[16] *J. Biol. Chem.*, **44**, 132 (1920).

[17] *Science*, **56**, 650 (1922).

[18] *J. Biol. Chem*, **57**, 415 (1923).

Comparative Analysis (*Concluded*)

1923	Vitovim Female No. 1235 G.	Vitovim 7 Young G.	100% Whole Wheat Bread Female No 1236 G.	100% Whole Wheat Bread 6 Young G.	Ordinary Good White Bread Female No. 1237 G.	Ordinary Good White Bread 6 Young G.
3/14	148	175	123	(3/18, 4 died) 192	147	220
3/21	120	195	134	(3/19, 2 died) All dead	152	223
3/28	108	222	134		151 (4/1, 1 died)	218
4/4	104	258	133		145	195 (5)
4/11	113	297	131		135 (4/15, 1 died)	190
4/18	132	336	129		131 (4/20, 1 died) (4/21, 1 died)	132
4/25	148	383	130		132 (4/27, 1 died)	67 (2)
5/1	153	447	130		123	29 (1)
5/9	153	566	131		138	All dead
5/16	155	652	130		156[a]	
5/23	154	691	129		174	
5/29	163	777	129		175	
6/6	174	897	129		174	
6/13	181	882	133		174	
6/20	185	932	139		180	
6/27	180	952	133		171	
7/3	178	969	137		172	
7/11	177	1017	139		177	
7/18	170	1030	142		174	
	Female No. 1235 (1st generation) was born to female No 763 and had young (7) on Sherman's Normal		Female No. 1236 (1st generation) was born to female No. 763 and had young (6) on Sherman's Normal		Female No. 1237 (1st generation) was born to female No. 763 and had young (6) on Sherman's Normal	

Sherman's Normal Diet consists of:

	Parts
Whole wheat	66²/₃
Dry whole milk	33¹/₃
Salt	1¹/₃

[a] Diet changed to Vitovim bread.

were placed on a diet of Vitovim bread to see if this bread would adjust the deficiency in the diet. The young made a remarkable recovery soon after the change.

Chart I shows this result in graphic form. It will be noted that the mother was able to gain in weight on this diet and showed no ill effects. The young, though not losing in weight, showed the lack of vitamin B.

Tests of a Complete or Perfect Food

The only method which scientific experimenters have at the present time for determining the relative nutritive value of different foods is that of conducting actual feeding tests upon growing, young animals, which may be kept under strict observation and experimental care. Such experiments are now accepted as the standard method for determining the biological nature or the nutritive value of foods. When conducted properly, these experiments yield remarkably concordant, reliable, and trustworthy results.

The following tests will accurately determine whether or not any food is a complete or perfect one:

1—Will it support normal and healthy growth in experimental animals?
2—Will it enable the test animals to reproduce normally and regularly?
3—Will it enable the mothers to nurse and raise their young?
4—After weaning, will it enable the young to grow normally to full maturity?
5—Will it enable those young to reproduce normally for successive generations?
6—Will it enable test animals, which have been debilitated because of being fed on deficient diets, to return to nearly perfect or normal health?

These same tests have been applied to Vitovim, the super white bread. Through them it is convincingly shown that this bread contains (*a*) adequate carbohydrates, (*b*) adequate and well-balanced proteins, (*c*) proper and sufficient mineral salts, (*d*) adequate content of vitamin B, and (*e*) adequate content of vitamin A.

This is a white bread, a bread of that degree of lightness demanded by the American public. The best white wheat flour is used in the manufacture of the loaf. To build up the quality and quantity of its protein, larger quantities of rich whole milk are used. In fact, rich whole milk is the only liquid used in the dough batch. In order to add still further milk, whole milk solids dried by the roller process are added. Never before has a bread so rich in milk been made.

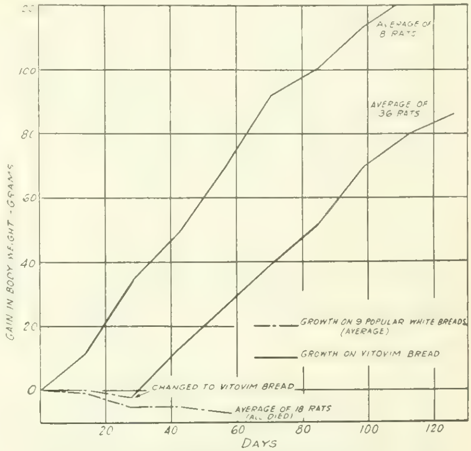

Chart 8—Growth of Animals Fed on Vitovim Bread Compared with That of Animals Fed on Nine Most Popular White Breads

Even with such a large amount of milk in the loaf it did not have a sufficiency of the vitamin B factor. Large quantities of a dry extract rich in vitamin B, proteins, and mineral salts prepared from the germ of the wheat are added to build up the vitamin B factor. Even with all the milk, the soluble extract from the germ of the wheat, and the high quality flour, there was still an improper mineral salt balance. Lime salts were further added to balance the phosphates of potassium, sodium, and magnesium.

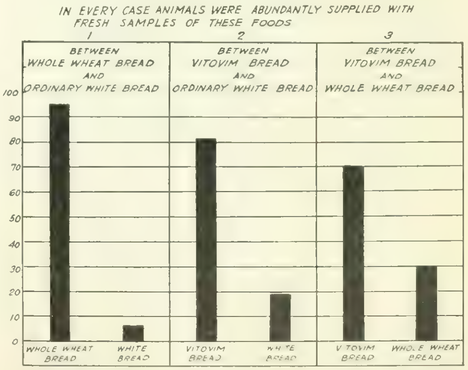

Chart 9—Relative Amounts of Breads Eaten when Animals Are Allowed to Choose. Natural Instinct Guides Animals Unerringly to the Food That Is Best for Them

This combination of ingredients properly proportioned and selected by the scientific men in the laboratory and skilfully handled by expert bakers has produced in Vitovim bread a super-food.

CONCLUSION

Vitovim bread when fed as the sole food produces normal growth and health in young test animals. Already eight generations of mice and five generations of albino rats have been reared on this bread and water. When animals are allowed free choice between breads of various kinds—white, whole-wheat, and Vitovim—natural instinct guides them to the more nourishing Vitovim loaf. In a 6 weeks' test it was found that animals selected Vitovim for 59 per cent of their diet, whole-wheat bread for 27 per cent, and ordinary white bread for only 14 per cent. This is already being duplicated in the case of children, where the child is naturally selecting more of Vitovim bread in preference to other bread.

The Vitovim bread is being fed to children in private homes and in institutions under competent direction. Observations are also being made with the ordinary bread. Both groups are given the same diet with the exception of the bread. The results confirm the conclusions derived from the animal feeding experiments. The groups receiving Vitovim bread as a part of their diet are making uniformly greater gains in height and weight than children of the same age and under the same conditions of the experiment but whose diet contains the ordinary bread.

ACKNOWLEDGMENT

This work was authorized and carried out under the sympathetic backing of George S. Ward, president of the Ward Baking Company. Due credit is here given to all the men in the laboratory, and to R. M. Allen, director of the Research Products Department, for the helpful suggestions and coöperation they have given toward the completion of this work.

A Rapid Method for the Analysis of Soap Powder[1]

By Fred F. Flanders and Anna D. Truitt

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THE routine examination of a large number of samples of soap powder by means of the separation of soap from alkaline salts, based on the solubility of soap in 95 per cent alcohol,[2] has shown the method to be unsatisfactory in several respects. It is very slow and tedious because of the repeated dryings and weighings necessary, and, as pointed out by Low,[3] is subject to defects inherent in the supposition that all the soap dissolves in the alcohol while the alkaline salts remain in the insoluble portion.

The writers have corroborated Low's findings that even with absolute alcohol some sodium carbonate dissolves. They have also demonstrated that the residue will often contain much more than traces of soap. By applying corrections for these factors when dealing with soap powders made up of soap and sodium carbonate, very good results are obtainable, but at the additional expense of much time and labor. The writers have worked out a method by means of which weighings are avoided entirely, the whole operation being conducted by titration on the same 2-gram sample. It appears to be quite as accurate as the old method, and is much more rapid, requiring little more than an hour for a complete analysis. The method is based on the titration of total alkali, with subsequent extraction and titration of the fatty acids in chloroform solution. The separation of soap and sodium carbonate is thus accomplished in a chemical instead of in a physical way.

PROCEDURE

Weigh accurately 2 grams of sample and transfer to a 400-cc. beaker. Add 100 cc. of hot water and heat to obtain a clear solution. Titrate while hot with 0.5 N hydrochloric acid, using methyl red as indicator. After the end point is reached, add 2 cc. excess of 0.5 N hydrochloric acid, several pebbles to prevent superheating, cover with a watch glass, heat to boiling, and boil gently 10 minutes to remove carbon dioxide. Titrate back to end point with 0.1 N sodium hydroxide. Add 2 cc. excess of 0.5 N hydrochloric acid, cool, and transfer to a separatory funnel. Extract with three portions of chloroform, using 25 cc. for each extraction, first rinsing the beaker with each portion. Draw off chloroform through a dry filter into a dry Erlenmeyer flask. Wash filter with 25 cc. chloroform to remove traces of fatty acids. Heat to boiling and boil gently 5 minutes to remove carbon dioxide (pebbles should be added before heating to prevent superheating). Titrate the fatty acids while still hot with 0.1 N sodium ethylate, using 5 drops of phenolphthalein indicator made up in absolute alcohol (1 gram = 100 cc.). The titration should be conducted quite rapidly and carried to the first permanent red color.

CALCULATION

$$\frac{(\text{Cc. } 0.5\ N\ \text{HCl}) - (\text{cc. } 0.1\ N\ \text{NaOH}) - (\text{cc. } 0.1\ N\ \text{C}_2\text{H}_5\text{ONa}) \times 0.0053}{2} = \text{Na}_2\text{CO}_3$$

$$\frac{(\text{Cc. } 0.1\ N\ \text{C}_2\text{H}_5\text{ONa}) \times 0.0306}{2} = \text{anhydrous soap}$$

PREPARATION OF REAGENTS

The sodium ethylate is prepared by dissolving 2.3 grams of cleaned metallic sodium in 1 liter of absolute alcohol.[4] It is standardized against ordinary 0.1 N hydrochloric acid, using phenolphthalein as indicator. As absolute alcohol has a rather large coefficient of expansion, it should be restandardized at the temperature at which it is used when that varies more than a degree from the temperature at which standardization last took place. If a precipitate appears in the ethylate it should be filtered.

The chloroform should be tested for acidity by adding indicator to 100 cc. and titrating with ethylate; if more than a single drop is required to give a strong end point, the chloroform must be washed in a separatory funnel with dilute sodium hydroxide. After the layers have separated well it should be filtered through a dry filter. Dry flasks must be used in the chloroform titration, as a single drop of water will entirely vitiate the results.

The factor selected, 0.0306, is the mean between the molecular weights of sodium oleate and sodium stearate. By making a moisture determination the results may be checked against 100 per cent. Owing to the presence of small amounts of sodium chloride and sodium sulfate, and sometimes unsaponified fat, in soap powders made up of soap and soda ash, the results will generally add up to 98 or 99 per cent.

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[1] Received May 28, 1923.

[2] *Bur. Standards, Circ.* **62**, 2nd ed., p. 31.

[3] THIS JOURNAL, **11**, 1169 (1919).

[4] Folin and Flanders, *J. Am. Chem. Soc.*, **34**, 774 (1912).

The Lubricant and Asphaltic Hydrocarbons in Petroleum[1]

By Charles F. Mabery

Case School of Applied Science, Cleveland, Ohio

This work is a study of the hydrocarbons in petroleum which cannot be distilled without decomposition. The method used for their separation was fractional solution in a hot mixture of ether and alcohol, after first distilling the crude oil to 300° C., first separating the homologs of each series and then dividing the series into fractions. Identification of the hydrocarbons was then accomplished by determination of specific gravity, molecular weight, and percentage composition.

This method of separation and analysis was applied to five crude oils, from West Virginia, Pennsylvania, Ohio, Texas, and Russia. The Ohio oil being one of peculiar composition, a study of its distillable constituents as well as of its fractions separated by solution is given. The homologs of the heavier series above 300° C. vacuum appear to increase regularly and are divided into (1) the D hydrocarbons, lubricants to the final heavy ends, and (2) the H group, asphaltic in the heavy ends. A comparison of the various oils shows a well-defined distinction between the lubricant and the asphaltic hydrocarbons, and the higher specific gravity of the Texas and Russian lubricant hydrocarbons is due to their inherent structure. The wide variation in specific gravity of individual fractions of the heavy crudes indicates the presence of carboxyl acids or esters. Iodine number determinations show that only the ring form of unsaturation applies to the lubricant hydrocarbons, and they do not appear to enter into the formalite reaction as applied by the Marcusson method.

Although much time has been devoted in this laboratory to the composition of the distillable hydrocarbons in petroleum, no attention has hitherto been given here and little elsewhere to the identification of the hydrocarbons that cannot be distilled without decomposition. Of the few attempts to separate these constituents of petroleum by cold solution and precipitation, "cold fractionation," the most noteworthy is the work of Charitschoff, who described the following hydrocarbons with their specific gravity: $C_{19}H_{38}$, 0.8930; $C_{21}H_{40}$, 0.9050; $C_{22}H_{42}$, 0.9080; $C_{24}H_{46}$, 0.9130; $C_{35}H_{68}$, 0.9150; and it has doubtless suggested the frequent allusions to the presence of naphthene lubricants in American petroleum. However, none of the hydrocarbons from Baku oil, described in this paper, contain the series C_nH_{2n}, nor the C_nH_{2n-2}, although some of these specific gravities are about the same as those of the series C_nH_{2n-8} in Baku oil, to be described later, and none of the varieties of American petroleum have shown such composition.

Since petroleum hydrocarbons begin to decompose in distillation at about 200° C., and above 300° C. most crude oils, even under pressures reduced to 20 mm., show evidence of decomposition, it is impossible to separate the constituents of petroleum by any form of distillation that will not distil at 300° C. vacuum.

Separation by Fractional Solution

With the exclusion of distillation the only remaining possibility appeared to be fractional solution, and, in view of the variations in other physical constants, there seemed to be no reason why the different series and homologs should not possess sufficient differences in solubility to permit their approximate separation in this manner. Trial of the various solvents excluded all but a mixture of ether and ethyl alcohol, and since all the constituents of petroleum dissolve freely in ether, but are quite insoluble in alcohol, it seemed possible to prepare from them a convenient solvent. For general use a mixture of equal parts by volume, with suitable variations for the more soluble lighter ends, and the less soluble constituents of the heavier ends proved efficient for all the varieties of crude oil. For convenience of reference, the lighter fractions will be referred to as the "higher" or "upper ends," and the heavier as the "lower ends" of the series or group.

Under a pressure of 30 mm. the crude oil was first distilled to 300° C. For the removal of the paraffin hydrocarbons from the Appalachian oils, the solid residue was dissolved in ether to a dilute solution, alcohol added until the paraffin began to participate flocculent, the solution cooled to 0° C., filtered cold, again cooled to −20° C., and again filtered, with very little paraffin remaining in the oil after the first filtration. There is some difficulty in reaching the point where flocculent precipitation begins without carrying down a large amount of the semisolidified oil.

Homolog Separation

In lots of 1000 to 1500 grams the vacuum residue, free from paraffin, was heated to the boiling point of the solvent in flat, cork-stoppered bottles in a hot water bath with frequent shaking, the stopper being held in with the finger and frequently removed to relieve excessive pressure. For collection of the homologs of all the series into ten or fifteen groups, the hot solution was poured off from each extraction and the solvent distilled, the first fractions containing the more soluble upper end, and the diminishing solubility giving the consecutive fractions down to the last residue. For further separation of the series homologs, the lowest group was first heated with the solvent of proper concentration, sufficient to dissolve a considerable part, and the hot solution poured off, cooled, and again poured off from the separated oil. To this was added the next fraction, which was again heated, and the solution poured off for the treatment of the next fraction. This procedure was continued to the upper end. The solvent distilled off from the last treatment gave the first member of the group, and this procedure was repeated six times. Since the specific gravities of the fifth and sixth fractions were approximately the same, it was assumed that the homologs of all the series were fairly well collected within the respective groups. The efficiency of this method appeared in the differences in consistency between the lowest fractions, extremely thick, viscous, or nearly solid lubricants, as in the Appalachian oils, or thick, black, tarry or solid asphalts, as in the Texas and Russian oils, and the upper fractions, thin, amber-colored lubricants.

Series Separation—Beginning at the lower end of the group each fraction was about half dissolved in rich, hot solvent, decanted, leaving a residual oil, *H*, the solvent distilled, giving another residual oil, *D*, and this was continued with all the fractions to the upper end. To be sure that a single extraction gave an approximate separation, it was followed by another similar treatment, giving two series, *Da* and *Db*. The specific gravities of *a* and *b* proved to be sufficiently concordant to indicate a fairly satisfactory separation by the first treatment.

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[1] Received December 4, 1922

In a second mode of series separation each of the first group fractions was heated to boiling with the solvent, the hot solution decanted, cooled, again poured off from the separated oil and distilled, giving three oils—*H*, the first residue; *C*, the residue from cooling; and *D*, the residue from the distilled solvent. Each of these oils was again treated in a similar manner, and this treatment continued three or four times, thus dividing the original oils into eight or twelve fractions, did not materially change the specific gravity from the results of a single cross separation, from which it was inferred that the marked difference in solubility gave a fairly good separation in the first extraction. The following examples of its application on some of the oils as a means of control show the rapid separation by this method. A top fraction of a Russian vacuum residue containing more soluble, heavier carboxyl constituents brought up from below, and another from the Rosenbury oil, were separated by a single extraction into light and heavier constituents, as follows:

Russian fraction, specific gravity 0.9236	0.9594 *H* residue, hot 0.9198, *C* residue, solvent cooled 0.8925, *D* residue, solvent distilled
Rosenbury (Pa.), specific gravity 0.9064	0.9230, *H* 0.8908, *C* 0.8875, *D*

No doubt the petroleum hydrocarbons under the condition of cold solution used by Charitschoff do exert a mutual solubility and interfere with the use of specific gravity as means of identification, but under the influence of a hot solvent it seems to be quite otherwise.

The constants relied upon for grouping and identification were specific gravity, molecular weight, and composition by analysis. Determinations of specific gravity, except of the most viscous tars, which were weighed under water by the method of Kirschbraun, were made in a Sprengel pycnometer at 20° C.

In the beginning, molecular weights, especially of the heavy hydrocarbons, gave much trouble. Of the common solvents benzene alone at the boiling point was applicable, and this was reliable only with the lower members of the Appalachian oils. Stearic acid at 50° C. proved to be more satisfactory. A weight of oil from 0.3 to 1.5 grams, depending upon the specific gravity of the oil, gave a depression of from 0.150 to 0.400° C. on the Beckman scale. The limitations of the method and the accuracy required for concordant readings are shown by the fact that for molecular weights above 1000, a depression of 0.001° C. corresponds to nearly a difference of the increment, CH_2, but below 500 to a difference of only 2 to 4 units. Occasionally, stearic acid gives abnormally high readings, doubtless caused by irregularity in the initial separation of crystals, which resisted all attempts toward correction by variation in stirring or other manipulation; but several, usually not more than three repetitions, readily revealed by concordant values, could be relied upon for the desired results. In the extremely high values, 1600 or more, that define the hydrocarbons with the largest molecular weights, the observations were as closely concordant as with the oils having a molecular weight of 300. The commercial acid dried at 100° C. is sufficiently pure; different lots showed small variations in the constant—for example, (1) 4.431, (2) 4.467; Bernstein gives for this constant, 4.5. Particular attention was necessary in getting complete solution of the heavy oils, and these required large weights for sufficient depression.

To yield the small differences in percentages of carbon and hydrogen necessary to distinguish between the different series, the gases from the asphaltic oils require the highest temperature for complete combustion that the most infusible glass will stand with a stream of oxygen on the copper oxide in front of the oil. Much time was saved by weighing the bulbs filled with oxygen. Although a 50 per cent solution of potassium hydroxide was used, with solid potassium hydroxide or soda lime and phosphorous pentoxide in the safety tube of the Geissler bulb, a horizontal tube in front with soda lime and phosphorous pentoxide invariably showed from 0.0005 to 0.0020 gram increase in weight, sufficient, if lost, to spoil the analysis.

VARIETIES OF PETROLEUM INVESTIGATED

General application of the method herein described to the petroleum fields of the world should doubtless involve the study of more than one hundred representative varieties. In this paper is included the separation of the constituent hydrocarbons from the following five typical crude oils:

TABLE I

LOCALITY	STRATA	Depth of Well Feet	Specific Gravity	Percent 300° C. Vacuum Residue	Specific Gravity 300° C. Vacuum Residue
Cabin Creek, W. Va.	Lowest Berea grit				
1st sample		1700	0.8100	25	8683
2nd sample		1700	0.7850	20	8638
Rosenbury, Emblenton, Pa.	Rosenbury sand	1240	0.8080	35	8852
Mecca, Ohio	Loose sand	150	0.9023	80	9076
Sour Lake, Texas	Loose sand	2000	0.9333	40	9580
Baku, Russia	Loose sand	Shallow	0.8650	35	9270

The Cabin Creek and Rosenbury oils are regarded as the best varieties of Appalachian petroleum, and known in the trade as paraffin-base oils. They contain large proportions of the gasoline, kerosene, and solid paraffin hydrocarbons, leaving residues solid with paraffin at 300° C., 30 mm. Authentic specimens of these oils, pale yellow in color, were procured for this examination from O. C. Dunn, Marietta, Ohio.

The Sour Lake oil, procured from a reliable source, is a typical heavy Southern crude, containing no C_nH_{2n+2} hydrocarbons; the crystalline hydrocarbons occasionally observed in some distillates are probably of a heavier series. That the less volatile portions of the Texas oils are composed to a large extent of the best lubricant hydrocarbons cannot be doubted, and while the balance of the Northern crudes are of the lighter series, a large proportion in the basic Southern crudes are of the so-called asphaltic hydrocarbons which impart high viscosity to the lubricants containing them. How far the higher specific gravity and viscosity indicate superior lubricant quality depends, of course, on the inherent wearing quality of the asphaltic hydrocarbons, and this has never been precisely defined. In the early development of Texas oil territory it was the synonym for high sulfur petroleum. Intimately associated with beds of sulfur, the sulfur was dissolved to the limit of saturation, and the resulting chemical changes eliminated hydrogen as hydrogen sulfide with the formation of the heavy hydrocarbons. In the formation of such heavy crudes as the Sour Lake, evidently sulfur has been a determining element. With continued production the original proportions of sulfur in these oils, 1 to 3 per cent, have been greatly reduced.

The Russian oil is a part of two barrels brought for the author's use twenty-five years ago from Baku. It is less stable than American oils and care is necessary to avoid decomposition, even under reduced pressure. Like all Russian crudes, the distillable portion is composed of the naphthene hydrocarbons that make superior luminants, and the remainder has a smaller proportion of lubricants than American petroleum, but considerable asphaltic constituents. The great body of the midcontinental fields yields oils with mixed constituents; they are usually referred to as oils with a mixed base, paraffin and asphaltic, and the lubricants made from them possess a peculiar composition and quality quite different from those of the Appalachian or the Southern crudes. From the general composition of these varieties of petroleum,

TABLE II—DISTILLABLE CONSTITUENTS OF MECCA PETROLEUM

Fraction ° C.	Specific Gravity	DETERMINATIONS Mol. Wt.	DETERMINATIONS C %	DETERMINATIONS H %	Hydrocarbon	REQUIRED Mol. Wt.	REQUIRED C %	REQUIRED H %	Series	Refractive Index
120–121	0.8600	177	86.61	13.26	$C_{13}H_{24}$	180	86.66	13.34	C_nH_{2n-2}	1.4605
130–131	0.8631	190	86.67	13.23	$C_{14}H_{26}$	194	86.60	13.40	C_nH_{2n-2}	1.4625
138–141	0.8648	204	86.62	13.33	$C_{15}H_{28}$	208	86.54	13.46	C_nH_{2n-2}	1.4650
150–152	0.8692	218	87.10	12.75	$C_{16}H_{28}$	220	87.28	12.72	C_nH_{2n-4}	1.4665
168–170	0.8696	226	86.87	12.85	$C_{17}H_{30}$	234	87.18	12.82	C_nH_{2n-4}	1.4715
182–184	0.8722	244	87.08	12.82	$C_{18}H_{32}$	248	87.10	12.90	C_nH_{2n-4}	1.4710
194–196	0.8730	258	86.95	13.12	$C_{19}H_{34}$	262	87.03	12.97	C_nH_{2n-4}	1.4725
213–214	0.8750	270	86.90	12.95	$C_{20}H_{36}$	276	86.96	13.04	C_nH_{2n-4}	1.4750
237–238	0.8834	334	86.65	13.24	$C_{24}H_{44}$	332	86.75	13.25	C_nH_{2n-4}	1.4785
244–246	0.8840	348	86.73	13.21	$C_{25}H_{46}$	346	86.70	13.30	C_nH_{2n-4}	1.4815
Light Hydrocarbons from Mecca Vacuum Residue										
	0.8837	343	86.62	13.25	$C_{25}H_{46}$	346	86.70	13.30	C_nH_{2n-4}	
	0.8847	389	86.70	13.25	$C_{28}H_{52}$	388	86.60	13.40	C_nH_{2n-4}	

they seemed especially well adapted for this investigation, as representing the principal fields.

Mecca petroleum, specific gravity 0.9023, known as a natural lubricant since the beginning of the petroleum industry, is typical of occasionally occurring small pockets or sections at shallow depths where the original oil has been partially refined by natural agencies, leaving only hydrocarbons with large molecular weights, containing no gasoline, kerosene, or paraffin hydrocarbons and a very small amount of the asphaltic hydrocarbons. All but 12 per cent of the lighter end form the best lubricants.

DISTILLABLE CONSTITUENTS OF MECCA PETROLEUM

On account of its peculiar composition, and since there is an opportunity, for the first time, to give a description of the undecomposed hydrocarbons in a crude oil from beginning to end, it seemed of interest to make the separation of Mecca oil complete from the first distillate. The lower constituents were, therefore, separated by several distillations *in vacuo*, refined, and the values obtained for specific gravity, molecular weight, and percentage composition are given in Table II. The peculiar disagreeable odor of some of the distillates indicates that the crude oil is not so far removed from its original organic source as the Appalachian oils.

These determinations of refractive index increase with increase in specific gravity and in molecular weight the opposite of the hydrocarbons in the Appalachian oils, and, as will appear later, even in the Mecca hydrocarbons of higher molecular weight in the vacuum residue. The distillate 244° to 246° C., specific gravity 0.8840, treated as in the separation of the *D* and *H* series, gave a *D* hydrocarbon, specific gravity 0.8850, refractive index 1.4865; and an *H* hydrocarbon, specific gravity 0.8835, a lower refractive index, 1.4765, both indicating more than one series, as in the higher hydrocarbons. Some of the Mecca vacuum residue that can be distilled at 300° to 320° C. without decomposition, and that has been refined for use as a lubricant on fine watch and clock bearings, was separated by the solvent into the following fractions:

Fraction	Specific Gravity	Index of Refraction
1–*D*	0.8837	1.4835
1–*H*	0.8780	1.4805
2–*D*	0.8789	1.4815
2–*H*	0.8710	1.4765
3–*D*	0.8705	1.4815
3–*H*	0.8682	1.4755
4–*D*	0.8745	1.4785
4–*H*	0.8680	1.4760
5–*D*	0.8750	....

The molecular weight and analysis gave the following formulas for the *D* group, indicating the series C_nH_{2n-4}:

$C_{21}H_{38}$
$C_{22}H_{40}$
$C_{24}H_{44}$
$C_{26}H_{46}$
$C_{28}H_{52}$

These hydrocarbons form the connecting link in the series between those that can and those that cannot be distilled. The data of this examination indicate more than one series.

SERIES AND HOMOLOG HYDROCARBONS IN PETROLEUM

Investigations carried on in this laboratory and elsewhere have shown that petroleum is chiefly composed in variable proportions of the series C_nH_{2n+2}, gasoline, kerosene, and paraffin hydrocarbons; the series C_nH_{2n-2}, the light lubricants, especially of Appalachian petroleum; the series C_nH_{2n-4} and C_nH_{2n-8}, the heavier lubricants, the aromatic derivatives of benzene; and heavier series still poorer in hydrogen to C_nH_{2n-20} than appear in this paper are reported as present in European petroleum. The homologs of the heavier series above 300° C. *vacuo* appear to increase in regular increments similar to the distillable series—the *D* hydrocarbons, lubricants to the final heavy ends, except in the asphaltic crudes, and the *H* hydrocarbons, asphaltic in the heavy ends—in all except the Appalachian petroleum.

In the upper ends of the series first separated of all the oils examined, the specific gravity of the fractions increased very materially, some even higher than those of the lower ends. This was found to be caused by carboxylic acids or ethers more soluble than the hydrocarbons themselves. By further treatment of the upper fractions, the soluble oils were removed, leaving the hydrocarbons in Table III. The first ten to fifteen *D* and *H* homologs separated in each crude oil were given two or more extractions and collected in the smaller groups presented in this table. Much time was lost in this work before it was learned that the crude oils contained more than one series of lubricants, and that the series as well as the individual homologs differed materially in solubility. While the formulas and series represent the definite composition of the fractions separated, it should require the manipulation of much larger quantities of the crude oils than is possible in the ordinary chemical laboratory, and, as in fractional distillation, a greatly prolonged treatment to isolate with a closer approximation the individual hydrocarbons. To avoid serious loss in watch-glass transference, the fractions were kept in bottles saturated with the solvent and small lots were dried at 120° C. for examination.

For the purpose of showing at a glance the consistency of the hydrocarbons described in the preceding table as they appear spread out on watch glasses, in Table IV is given a brief description of the first and last members of each series from all the crude oils.

In the destructive distillation of Appalachian petroleum by the common method of refining, the most valuable lubricants of the heavy ends, such as the last *D* and *H* fractions in the Cabin Creek, Rosenbury, and Mecca (Table III), the best lubricants in any petroleum, are lost in coking. This is of less consequence in the asphaltic oils, for the lubricants in these crudes are for the most part carried over in the steam distillates, leaving only asphaltic residues.

On account of the less solubility of the lower members of each series and the separation of homologs in only one direction, it was possible to remove very completely the higher homologs, and, therefore, to obtain data for the calculation of the formulas of the lowest residual hydrocarbons as reliable as the methods of definition are capable of yielding. These last hydrocarbons were, therefore, carefully purified for the comparison of physical properties and lubricant value. Those from the heavier oils have the intensified qualities of the commercial asphalts; black in color, they may be drawn

TABLE III

Fraction	Specific Gravity	Determined Mol. Wt.	Determined C Per cent	Determined H Per cent	Formula	Calculated Mol. Wt.	Calculated C Per cent	Calculated H Per cent	Series	Refractive Index
					Cabin Creek					
D Series										
1	0.8755	309	86.76	13.21	$C_{22}H_{40}$	304	86.84	13.16	C_nH_{2n-4}	1.4920
2	0.8764	327	86.76	13.18	$C_{24}H_{44}$	332	86.75	13.25	C_nH_{2n-4}	....
3	0.8815	428	86.56	13.34	$C_{31}H_{58}$	430	86.50	13.50	C_nH_{2n-4}	....
4	0.8822	452	86.45	13.44	$C_{33}H_{62}$	458	86.46	13.54	C_nH_{2n-4}	....
5	0.8829	488	86.32	13.48	$C_{36}H_{66}$	486	86.42	13.58	C_nH_{2n-4}	....
6	0.8832	585	86.35	13.59	$C_{42}H_{80}$	584	86.30	13.70	C_nH_{2n-4}	....
7	0.8835	717	86.10	13.79	$C_{52}H_{100}$	724	86.20	13.80	C_nH_{2n-4}	1.4880
8	0.8855	803	86.27	13.73	$C_{58}H_{112}$	808	86.14	13.86	C_nH_{2n-4}	1.4810
H Series										
1	0.8721	459	87.21	12.70	$C_{33}H_{58}$	454	87.22	12.78	C_nH_{2n-8}	1.4880
2	0.8725	476	87.20	12.64	$C_{34}H_{60}$	468	87.20	12.80	C_nH_{2n-8}	....
3	0.8729	490	87.02	12.86	$C_{36}H_{64}$	496	87.10	12.90	C_nH_{2n-8}	....
4	0.8819	635	86.52	13.51	$C_{46}H_{84}$	636	86.79	13.21	C_nH_{2n-8}	....
5	0.8863	750	86.72	13.22	$C_{54}H_{100}$	748	86.64	13.36	C_nH_{2n-8}	1.4870
6	0.8873	769	86.72	13.42	$C_{55}H_{102}$	762	86.60	13.40	C_nH_{2n-8}	....
7	0.9063	1696	86.50	13.43	$C_{122}H_{232}$	1700	86.32	13.68	C_nH_{2n-12}	1.4810
					Rosenbury					
D Series										
1	0.8796	384	86.13	13.40	$C_{28}H_{52}$	388	86.60	13.40	C_nH_{2n-8}	1.4930
2	0.8816	438	86.68	13.24	$C_{32}H_{60}$	444	86.48	13.52	C_nH_{2n-8}	1.4890
3	0.8822	481	86.42	13.39	$C_{36}H_{66}$	486	86.42	13.58	C_nH_{2n-8}	....
4	0.8836	518	86.15	13.71	$C_{37}H_{70}$	514	86.38	13.62	C_nH_{2n-8}	1.4880
Series										
1	0.8742	549	87.08	12.85	$C_{40}H_{72}$	552	86.96	13.04	C_nH_{2n-8}	1.4920
2	0.8765	615	86.78	13.15	$C_{45}H_{82}$	622	86.82	13.18	C_nH_{2n-8}	....
3	0.8812	639	86.65	13.25	$C_{46}H_{84}$	636	86.78	13.22	C_nH_{2n-8}	....
4	0.8850	666	86.60	13.30	$C_{48}H_{88}$	664	86.74	13.26	C_nH_{2n-8}	....
5	0.8848	727	86.59	13.29	$C_{52}H_{96}$	720	86.68	13.32	C_nH_{2n-8}	...
6	0.8865	805	86.63	13.37	$C_{58}H_{108}$	804	86.56	13.44	C_nH_{2n-8}	1 4870
7	0.8950	830	86.49	13.52	$C_{60}H_{112}$	832	86.54	13.46	C_nH_{2n-8}	....
8	0.8998	980	86.69	13.28	$C_{69}H_{126}$	954	86.80	13.20	C_nH_{2n-12}	....
9	0.9079	1730	86.58	13.35	$C_{125}H_{234}$	1734	86.50	13.50	C_nH_{2n-16}	1.4870
					Mecca					
D Series										
1	0.8945	465	87.37	12.61	$C_{34}H_{60}$	468	87.20	12.80	C_nH_{2n-8}	....
2	0.8950	500	87.13	12.70	$C_{36}H_{64}$	496	87.10	12.90	C_nH_{2n-8}	....
3	0.8960	631	86.87	13.10	$C_{46}H_{84}$	636	86.78	13.22	C_nH_{2n-8}	....
4	0.8962	662	86.60	13.20	$C_{48}H_{88}$	664	86.75	13.25	C_nH_{2n-8}	....
5	0.8966	728	86.62	13.22	$C_{53}H_{98}$	734	86.66	13.34	C_nH_{2n-8}	....
6	0.8982	770	86.41	13.50	$C_{56}H_{104}$	776	86.60	13.40	C_nH_{2n-8}	....
7	0.8998	832	86.45	13.47	$C_{60}H_{112}$	832	86.54	13.46	C_nH_{2n-8}	....
8	0.9171	1080	86.58	13.42	$C_{78}H_{148}$	1084	86.34	13.66	C_nH_{2n-8}	....
H Series										
1	0.9058	477	87.65	12.37	$C_{35}H_{58}$	478	87.87	12.13	C_nH_{2n-12}	....
2	0.9072	550	87.57	12.48	$C_{40}H_{68}$	548	87.59	12.41	C_nH_{2n-12}	....
3	0.9018	684	87.06	12.82	$C_{50}H_{88}$	688	87.21	12.79	C_nH_{2n-12}	....
4	0.9022	725	87.16	12.76	$C_{52}H_{92}$	688	87.16	12.76	C_nH_{2n-12}	....
5	0.9052	823	87.12	12.73	$C_{60}H_{108}$	828	86.96	13.04	C_nH_{2n-12}	....
6	0.9065	992	87.22	12.75	$C_{72}H_{128}$	992	87.10	12.90	C_nH_{2n-16}	....
7	0.9600	1662	87.34	12.56	$C_{122}H_{204}$	1668	87.23	12.77	C_nH_{2n-20}	....
					Sour Lake, Texas					
D Series										
1	0.9408	450	87.93	11.91	$C_{33}H_{54}$	450	88.00	12.08	C_nH_{2n-12}	1 4980
2	0.9467	462	88 09	11.81	$C_{34}H_{56}$	464	87.93	12.07	C_nH_{2n-12}	....
3	0.9482	503	87.82	12.15	$C_{37}H_{62}$	506	87.74	12.26	C_nH_{2n-12}	..
4	0.9535	531	87.58	12.30	$C_{39}H_{66}$	534	87.64	12.36	C_nH_{2n-12}	1 4960
5	0.9595	554	87.62	13.32	$C_{41}H_{70}$	562	87.54	12.46	C_nH_{2n-12}	.
6	0.9643	849	86.80	13.18	$C_{62}H_{112}$	856	86.92	13.08	C_nH_{2n-12}	1 4940
H Series										
1	0.9470	602	87.90	12.05	$C_{44}H_{72}$	600	88.12	12.00	C_nH_{2n-16}	1 4970
2	0.9497	630	87.60	12.45	$C_{46}H_{78}$	632	87.62	12.38	C_nH_{2n-16}	....
3	0.9559	680	87.55	12.35	$C_{50}H_{84}$	684	87.72	12.28	C_nH_{2n-16}	....
4	0.9643	716	87.58	12.25	$C_{52}H_{88}$	712	87.64	12.36	C_nH_{2n-16}	....
5	0.9700	792	87.66	12.25	$C_{58}H_{96}$	785	87.88	12.12	C_nH_{2n-20}	1 4940
6	0.9714	854	87.50	12.24	$C_{62}H_{104}$	848	87.74	12.26	C_nH_{2n-20}	...
7	0.9720	981	87.65	12.35	$C_{72}H_{124}$	988	87.45	12.55	C_nH_{2n-20}	....
8	1.0230	1239	87.60	12.27	$C_{90}H_{160}$	1240	87.98	12.02	C_nH_{2n-20}	....
					Baku, Russia					
D Series										
1	0.9186	381	87.42	12.53	$C_{22}H_{44}$	308	88.05	11.95	C_nH_{2n-10}	1.4920
2	0.9251	402	87.75	11.93	$C_{29}H_{48}$	396	87.88	12.12	C_nH_{2n-10}	....
3	0.9254	494	87.46	12.53	$C_{36}H_{62}$	494	87.47	12.53	C_nH_{2n-10}	....
4	0.9262	640	86.91	13.03	$C_{46}H_{82}$	634	87.06	12.94	C_nH_{2n-10}	....
5	0.9288	1022	87.29	12.68	$C_{74}H_{138}$	1026	86.55	13.45	C_nH_{2n-10}	...
H Series										
1	0.9025	300	87.95	11.96	$C_{22}H_{36}$	300	88.00	12.00	C_nH_{2n-8}	...
2	0.9160	334	87.98	12.01	$C_{24}H_{40}$	328	87.80	12.20	C_nH_{2n-8}	..
3	0.9167	378	87.36	12.53	$C_{28}H_{48}$	384	87.50	12.50	C_nH_{2n-8}	..
4	0.9150	420	87.28	12.60	$C_{31}H_{54}$	426	87.32	12.68	C_nH_{2n-8}	...
5	0.9162	460	87.29	12 66	$C_{33}H_{58}$	454	87.22	12.78	C_nH_{2n-8}	..
6	0.9242	661	86.72	13.21	$C_{48}H_{88}$	664	86.75	13.25	C_nH_{2n-8}	....
7	0.9360	847	86.63	13.30	$C_{61}H_{114}$	846	86.52	13.48	C_nH_{2n-8}	...
8	0.9402	1098	98.31	12.68	$C_{80}H_{140}$	1100	87.28	12.72	C_nH_{2n-20}	1 4910

out to a considerable length in very fine threads, and possess great adhesiveness. The residual lubricants from the Appalachian crudes, amber in color, greasy in feel, and of high viscosity, differ in appearance from the gray basic stocks of the midcontinental lubricants, which are doubtless to some extent mixtures with asphaltic bases.

On account of the limits of accuracy in the determinations of molecular weights mentioned above, the fractions with higher values, such as the Rosenbury fraction $C_{125}H_{234}$, may be incorrect by one or more increments CH_2, but by the determinations upon which it is based it must have a high value, for the fraction 9–*H*, specific gravity 0.8933, gave in two molecular weight determinations (1) 1722, (2) 1718; further fractioned with specific gravity 0.8943 it gave 1728; and still further fractioned with specific gravity 0.9079 it gave 1730. There appears, therefore, to be no doubt as to its high molecular composition. So also the molecular weight 1696 of the Cabin Creek 7–*H* fraction, specific gravity 0.9063, with the next largest value, appears to be correct, since it was separated from both specimens of the crude oil which gave fractions with the molecular weights (1) 1685, (2) 1690, and with analysis corresponding to the formula $C_{123}H_{232}$. Therefore, with methane as the first gaseous hydrocarbon and pentane as the first liquid, under ordinary pressure, passing

TABLE IV—CONSISTENCY OF *D* AND *H* HYDROCARBONS

CABIN CREEK	ROSENBURY	MECCA	SOUR LAKE	RUSSIAN
		D Series		
(1) Light amber; fine, light lubricant	(1) Light amber; fine light lubricant	(1) Light amber; fine lubricant	(1) Dark amber; just flows; good lubricant	(1) Dark amber; slow flow; good lubricant
(8) Dark amber; flows readily; heavy lubricant	(8) Dark amber, thick flow; heavy lubricant	(7) Dark amber; thick flow; heavy lubricant	(7) Black, sticky tar; no lubricant	(8) Black, sticky, asphalt, oil; no lubricant
		H Series		
(1) Light amber; like 1–*D*	(1) Thin flow; light lubricant	(1) Light amber; thicker than Cabin Creek and Rosenbury	(1) Dark amber; just flows; good lubricant	(1) Dark amber; thick flow; heavy lubricant
(8) Dark amber; thick, solid	(8) Dark amber; slow flow	(7) Black, sticky, tarry oil	(8) Black, brittle, solid asphalt	(8) Thick, black asphalt oil

through the several series of light and heavy liquids, through viscous lubricants and solid paraffin, the final lower end is reached in these oils, so viscous they will not flow at common temperatures, the heaviest lubricant hydrocarbons in Appalachian petroleum.

Although the Mecca *H* group is composed in general of much heavier hydrocarbons than those from the Appalachian oils, the lubricants in the lower end of its series are not very different from the others. The last *H* hydrocarbon, $C_{122}H_{204}$, specific gravity 0.9600, is not a lubricant but an asphalt. The last *D* hydrocarbon, $C_{78}H_{148}$, specific gravity 0.9171, is a true lubricant, viscosity 5461 seconds; and the last Rosenbury, 9–*H*, specific gravity 0.9079, viscosity 5248 seconds, water standard 2.4 seconds at 50° C., probably the highest viscosity of any petroleum hydrocarbons, not only indicates that lower specific gravity is characteristic of the best lubricants, but it defines the difference in lubricant quality between the hydrocarbons of the Appalachian and those of the heavy asphaltic crude oils, with the higher specific gravity of the latter. Furthermore, this Mecca asphaltic oil, 7–*H*, has nearly the same high specific gravity, 0.9600, as the Sour Lake *D* asphaltic oil, specific gravity 0.9643, which resembles all the others with which it is associated, except the higher homologs, which are lubricants. The last Sour Lake oil, 8–*H*, specific gravity 1.0230, $C_{90}H_{160}$, is a brittle asphalt, for which no lubricant quality can be claimed.

The predominating asphaltic nature of the Baku oil is equally well defined, although with smaller values in specific gravity than the Sour Lake. The last *H* hydrocarbon is a black, sticky asphalt, a little higher in viscosity than the Sour Lake, but the last 5–*D*, $C_{74}H_{138}$, also a black sticky oil, has a higher viscosity than any other in this or the Sour Lake groups. In the Baku oil, unlike the others, the *D* series, C_nH_{2n-10}, seems to be poorer in hydrogen and heavier than the *H* series. The latter appears to be composed of a large number of low molecular weight hydrocarbons, the upper lubricants, the lower asphalts. As in the Sour Lake oil, the asphaltic hydrocarbons, in part lubricants, appear to predominate; even the last *D* oils are asphaltic.

The halogens react with these hydrocarbons as readily as with those of lower molecular weights, and with the same brisk evolution of the haloid acid. At about 70° C. the action proceeds most satisfactorily, with complete solution of the oil in 4 or 5 hours. At higher temperatures complete solution may take place in 1 hour. There is a marked difference in the appearance of the products from the *D* and *H* hydrocarbons. On pouring into a large volume of water, all the nitro derivatives from the *D* hydrocarbons separate in a flocculent, finally crystalline form, those from the heavy *H* hydrocarbons, as sticky oils. The reactions of these bodies show them to be nitrocarboxylic acids. With the ammonium salt formed by solution in ammonium hydroxide silver nitrate precipitates the silver salt readily soluble in nitric acid. With tin and hydrochloric acid the nitro compound is reduced to the amino acid. Barium and lead salts are readily formed. Analysis showed a much lower molecular weight than that of the original oil. While the action of solvents indicated complex mixtures, it seemed possible by proper fractionation to separate individual constituents. A study of these derivatives will be continued.

A summation of the facts relating to the nature of these hydrocarbons that make up from 25 to 35 per cent of petroleum seems to present a well-defined distinction between the lubricant and the asphaltic hydrocarbons, and appears to support the view that the higher specific gravity of the Sour Lake and Russian lubricant hydrocarbons is due to their inherent structure, which is altogether different from the lubricant structure of the Appalachian oils. In further study now in progress of petroleum lubricants in general, including the midcontinental oils, the relation of high specific gravity and viscosity to wearing quality will receive attention.

SULFUR IN SOUR LAKE, RUSSIAN, AND APPALACHIAN HYDROCARBONS

All determinations of sulfur were made by combustion in oxygen, the most accurate and expeditious method for sulfur in oils, tars, and asphalts. The variation in the percentage of sulfur indicates that the solvent differentiates in the sulfur derivatives as in that of the hydrocarbons, the greater part appearing in the *H* series.

TABLE V—PER CENT SULFUR IN HYDROCARBONS

	D FRACTIONS			*H* FRACTIONS			Crude Oil Per cent
	1	3	6	1	4	8	
Sour Lake	0.33	0.27	0.57	0.67	0.48	0.66	0.59
Cabin Creek							0.05
Rosenbury							0.01
Mecca							0.08
Russian							0.15

CARBOXYL DERIVATIVES IN AMERICAN PETROLEUM

All previous records of individual fractions from the different varieties of heavy petroleum—Ohio, California, Texas, Russia, etc.—have shown wide variation and abnormally high values in specific gravity. So the different series from the heavy crudes described in this paper show similar variations. These observations indicate that the carboxyl acids, or more probably esters, are present in all varieties of American petroleum, but in variable amounts, from the traces detected in the Appalachian oils to 2 per cent indicated by combustions of the fractions in the Sour Lake asphaltic oil. In further testing for the presence of carboxylic acids, the upper *D* Sour Lake fractions, dissolved in ether and extracted with potassium hydroxide, the aqueous solution acidified and again extracted with ether, leaves on evaporation a considerable amount of the oily acid residue. The specific gravity of the hydrocarbon oil before and after the extraction of 4–*D* fraction was, respectively, 0.9642 and 0.9575. The action of the solvent in carrying up the carboxyl derivatives in the fractions of the Russian oil is plainly evident in the high specific gravity, 1.1050, of the oil extracted from the upper *D* fraction, and the composition of this fraction (C, 86.83; H, 10.41) as compared with a fraction in the middle of the series (C, 87.58; H, 12.45), viscosity of the first oil at 50° C. 317 seconds and of the second oil 2005 seconds, water equivalent 2.8 seconds.

The carboxyl oil dissolved out from Mecca 1–*D* fraction, specific gravity 1.0105, gave by combustion 86.70 per cent C, and 12.41 per cent H, with a difference of 0.89 per cent for O_2. The viscosity of this oil was 468 seconds as compared with the hydrocarbon $C_{120}H_{220}$, specific gravity 0.9171 at the lower end of the same series, viscosity 1073 seconds at 50° C., water equivalent 2.8 seconds. It would be of interest to isolate larger quantities of these oils and ascertain their composition.

Unsaturation as Shown by Iodine Numbers

Of the two forms of unsaturation, open chain and the ring, evidently only the latter applies to the lubricant hydrocarbons and it has received much attention with respect to this condition as shown by the iodine numbers. Iodine reacts indiscriminately on the *D* and *H* hydrocarbons without showing any consistent relation or differences, but with results much like those observed in distillates. Trial of the Johansen method that appears to reveal what has been regarded as addition is really substitution, not only disproved addition, but gave negative numbers to the extent of two to four units.

Formalite Reaction

The *D* hydrocarbons described in this paper do not enter into this reaction as applied by the Marcusson method frequently quoted in works on lubrication, and the *H* hydrocarbons of the Texas and Russian oils give variable mixtures with an indefinite composition. The Rosenbury fraction 3–*H*, specific gravity 0.8812, gave after the reaction, 0.8827; and the Russian fraction 4–*D*, specific gravity 0.9262, after the reaction, 0.9291. In no case could the reaction proceed unless the resulting increase in temperature was unchecked. No naphthene, C_nH_{2n}, lubricant hydrocarbons have appeared, and contrary to the statement of Marcusson, the hydrocarbons from American petroleum have shown a superiority in lubricant quality over those from the Russian oil.

Acknowledgment

The writer wishes to acknowledge the efficient aid which he has received in this work from his assistants, R. C. Knapp and George Grossman.

The Value of Sweet Potato Flour in Bread-Making[1]

By H. C. Gore

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IT WAS recently shown[2] that two widely grown commercial varieties of sweet potatoes, Nancy Hall and Porto Rico, are rich in diastase and that they retain their diastatic power when sliced, dried, and ground into flour. The diastatic power ranges from 200 to 500 Lintner. That in the southern sweet potato we have a source of diastase capable of competing with the cereal sources of this important enzyme is shown from a study of the economics of sweet potato production.

The present cost of growing sweet potatoes on southern farms is shown by Haskell[3] to range from 22 cents per bushel upward, depending on the yields, the higher yields (160 bushels per acre) being produced at the lower unit cost. Sweet potatoes are a sure crop, respond well to fertilizers, and their cultivation is well understood. The entire crop or any portion of it can be used as raw material for the production of sweet potato flour. In a normal season about 40 per cent of the crop overgrows—that is, the roots become so large (greater than 3.5 inches in diameter) that they are not in demand for table use. They are, however, acceptable for technical uses.

In preparing sweet potato flour the process required is very simple. It is not necessary to peel the potatoes; they should, however, be washed in order to remove adhering soil. They are then sliced and dried. In drying, an updraft drier has been found to give satisfactory results. The temperature employed should not exceed 50° C. The yield is one-third the weight of the potatoes taken.

Sweet potato flour imparts but little flavor to the mash. It does not liquefy starch so rapidly as barley malt. It has, however, much greater saccharifying power. Its uses in industry remain to be worked out. The most interesting development which has occurred thus far is the discovery of the fact that sweet potato flour can be used as a bread improver.[4]

A large number of experiments were run in which a series of mixtures with varying percentages of sweet potato flour with hard wheat flour was tested. The different percentages of sweet potato flour used were based on the weight of flour taken. The baking tests were made by the straight dough method, with the following formula:

	Grams per Batch
Flour	450
Salt	7
Sugar	16
Yeast	10
Water	Sufficient to produce a dough of proper consistency

The sweet potato flour was mixed with the liquid ingredients before the wheat flour was added. Before panning, 170 grams of dough were removed for expansion tests, the remainder being panned for baking.

It was found that a substantial increase in volume occurred when sweet potato flour was used. One and one-half per cent of sweet potato flour appeared to give the best results. In one test, which may be considered as typical, the volume of the control loaf was 2250 cc., whereas that of the loaf prepared from the mixture containing 1.5 per cent sweet potato flour was 2425 cc. The texture of the bread and its color and flavor remained fully up to the standard. These results have been confirmed by independent tests made in three commercial baking laboratories. There is, therefore, no doubt of the fact that sweet potato flour does give a substantial increase in volume when used as a bread improver.

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[1] Presented before the Division of Agricultural and Food Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] *J. Biol. Chem.*, **44**, 19 (1920).

[3] *U. S. Dept. Agr., Bull.* **648**.

[4] The baking tests herein reported were made by L. H. Bailey, of the Bureau of Chemistry, and Miss R. Leone Rutledge, formerly of the Bureau of Chemistry.

Internal Treatment of Boiler Water—Proper and Improper[1]

By D. K. French

Dearborn Chemical Co., Chicago, Ill.

Up to the present time all discussions of the treatment of water supplies for industrial purposes have been limited to reactions which occur at atmospheric pressures and at temperatures below that of boiling water; yet no such discussion can be complete without consideration of what is known as internal treatment applied directly in the boiler for the correction of the difficulties encountered in steam production. The lack of discussion of this phase of water treatment has been caused largely by the confusion in the minds of those interested with regard to properly and thoughtfully applied treatment with proprietary compounds for which marvels are claimed.

In the boiler itself, where temperatures and pressures are much higher than those under which the ordinary water-softening processes operate, reactions occur which may or may not be the same as those occurring outside the boiler. These reactions have been given careful study by the author of this paper, and the observations gleaned from the practical application of this method of treatment are set forth in the accompanying article. In addition to the principles on which such treatments act, the author discusses at some length the proprietary compounds which have done so much to discredit this method of treatment.

ROUGHLY, boiler problems involve scale formation, corrosion, and foaming—all serious and worthy of investigation and treatment for their control or elimination. Scale formation seemingly has attracted the most attention, possibly because its manifestations are most easily observed and its treatment follows more common chemical knowledge.

SCALE FORMATION

The use of lime and soda ash has been general for years, but knowledge of the defects of the process is equally general. Both carbonate of lime and carbonate of magnesia are soluble after even the best adjusted lime additions. Furthermore, in practice these reactions are far from theoretically complete, owing to the presence of other salts naturally in water. Stein[2] and Sperry[3] agree that ideal conditions rarely follow such treatment in practice, and stress the importance of certain assisting reactions.

In the boiler, however, reactions take place rapidly and at high pressures are very complete, as a result of which there is almost no water that will not form some scale, even after the best outside treatment, as most incrustants are pretty nearly insoluble at 100 pounds steam pressure. While outside treatment is clarifying the water, it is also removing certain impurities which in the boiler might react to decrease the very definite crystalline character in which these same incrustants will deposit and cement on the heating surfaces. Organic and vegetable matter will not react in the cold—in fact, it will hold back precipitation. In the boiler the results are quite different, and while its precipitating value is not high, it changes the boiler medium sufficiently to prevent crystalline separation and causes the deposition of the scale-forming salts in a largely amorphous condition. This amorphous precipitate is easily influenced by boiler currents, so that, instead of settling immediately, these impurities circulate under such conditions as to make possible the collection of a very large percentage, if not all, in mud drums or similar devices designed for just such purposes. From the mud drum the precipitation can be removed as easily and more completely than in the case of previous outside treatment. While this means complete precipitation in the boiler, it eliminates feed-line stoppage, pump troubles, etc., which invariably follow an incomplete or poorly adjusted outside treatment. With a carefully calculated concentration of organic materials in the boiler, crystalline separation can be prevented, and while the sludge may be objectionable, its removal is much easier than that of the crystalline deposits.

Furthermore, economy in precipitating chemicals is possible if the balance between them and the controlling organic matter is properly adjusted. A case in mind is that of a large municipal plant using Missouri River water. The incrustants vary from 12 to 16 grains per gallon, including 2.5 to 5 grains of calcium sulfate. Treatment is adjusted so that the dosage per 1000 gallons of water contains barely 25 per cent of the necessary reacting chemicals. These reagents are combined with organic materials, however, in such a way as to result in the existence at all times of a water in the boilers from which calcium sulfate is completely absent, in which the carbonates are reduced to 1.5 grains or less, and which contains a 2 to 5-grain excess of originally added reactive alkali. When properly diluted in the feed water, the chemical reactions are retarded, while boiler temperature and pressure effect most of the precipitation, under such control, however, as to make possible the continuous and complete removal of the sludge long before it has been allowed to assume a crystalline condition. Organic matter, properly applied, also has the effect of slowly changing old crystalline deposits to a less compact and more easily disintegrated form so as to make possible its slow removal without discontinuing boiler operation.

Such organic reactions as occur usually produce bulky precipitates relatively light for their bulk, which, while continuing to circulate, seem to have coagulating and clarifying properties. In this way, finely divided suspended matter which might otherwise be found later in scale is removed. Other chemicals exist, not of an organic character, which have this same effect and can be used satisfactorily when conditions indicate the undesirability of adding organic matter to the boiler. Silicate of soda is such a material, and it is frequently sold as a boiler compound. Used alone, its efficiency is very low. Furthermore, its action is very little understood, as most silicate of soda compounds are claimed by their sellers to treat the metal and not the water.

For internal treatment there exists an almost unlimited variety of combinations which can be adjusted either to react directly or, as is more apt to be the case, to take advantage of what the boiler is doing. By thus assisting and controlling precipitation it is possible with a small amount of material to bring about conditions which would require many times that quantity if added outside for visible purification.

CORROSION

Corrosion is a type of boiler trouble which is more easily controlled through internal treatment than is scale formation. Outside treatment increases, rather than decreases, the natural corrosive tendency of a water, through the re-

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[1] Received July 31, 1923.

[2] *J. Am. Water Works Assoc.*, **6**, 202 (1919).

[3] *Ibid.*, **6**, 215 (1919).

moval of certain protective impurities.[4] Frequently, outside treatment increases noticeably the soda salts, which, while not corrosive of themselves, will soon concentrate sufficiently to make possible distinct electrolytic corrosion. Dissolved gas is also an active cause of this type of trouble. While lime can remove dissolved carbon dioxide, none of the known inorganic treating chemicals seem to have any effect on dissolved oxygen. However, the alkaline tannates, properly adjusted, have the property of combining with these gases, especially oxygen.[5] Organic acid compounds added to high concentrations of alkali first cause a reduction of the excess alkali, retarding the possible tendency toward caustic embrittlement, and then in the alkaline combinations act both as an absorber of corrosive gas and an interfering agent in connection with probable electrolytic corrosion.

Where organic materials cannot be applied, the chromates and dichromates are frequently used, though the amount necessary to get results in an operating boiler is usually too high for economy.

Corrosion is frequently attributed to magnesium sulfate, magnesium chloride, calcium nitrate, etc., and as a rule when these salts exist in any material quantity the pH values are very noticeably below 7.0, and sometimes below 6.0, without any free acidity. Properly adjusted chemicals introduced into the boiler are much more effective and their neutralizing value is higher than when the same reactions are carried on outside at normal temperatures.

The effect of alkaline tannates in reducing the corrosive value of concentrated soda salts can be demonstrated by measurement of the hydrogen-ion concentration, as well as by chemical examination. The composition of water from the boiler after varying periods of operation, when using organic types of treatment, cannot be even approximated volumetrically as the organic matter present interferes with ionization or produces less active addition products of salts which would cause trouble largely in proportion to their activity as inorganic impurities.

FOAMING

A third type of trouble is foaming. Again internal treatment properly devised and applied has produced remarkable results, whereas outside treatment, aside from clarifying a water, has invariably stimulated, if not actually created, a tendency to foam. Foaming has been variously attributed to sodium and potassium compounds in concentrated solutions, suspended matter, organic impurities, boiler construction, and uneven load and pressure. The latter two factors no doubt stimulate the trouble, but the whole problem is one of surface tension, increased as the dissolved salts increase in concentration, and complicated by operating conditions and the physical character of the water. A muddy water may steam quietly, and a clear supply may foam beyond control. However, anything which will lower surface tension without creating complications will reduce foaming. On the same basis, clarifying of the water is also a help. Suspended matter provides the nuclei for steam bubbles which, if not able to break easily through the surface film, will raise the water level to a dangerous degree. Soluble inorganic salts and some organic compounds toughen this surface film, and the most serious foaming follows a combination of the two conditions.

Outside treatment offers absolutely nothing to control this trouble. On the other hand, any outside treatment using soda in any form tends to stimulate foaming through the increased amount of soda available for concentration. Moreover, the acknowledged incomplete precipitation of the carbonates of lime and magnesia ultimately furnishes suspended matter to increase steam bubble formation in even the clearest water.

In the field of organic internal treatment it is possible to produce and use compounds that will not only destroy the tenacity of the surface film, but supply a form of organic coagulant which will readily clarify the water and definitely retard foaming.

It is a well-known fact that castor oil alone of all the animal and vegetable oils possesses properties which, released under proper conditions, have a marked effect in controlling this trouble. The result has erroneously led to the impression that the use of oils, mineral as well as saponifiable, would stop foaming. This is not the case, as oil of any kind, as such, will invariably increase, rather than decrease, surface tension. Castor oil alone, or with improperly selected materials added, is absolutely without value; properly combined, the results are immediate and effective. In one particularly recent case of an enormous plant where an antifoam preparation was used following preliminary treatment and filtration through a treating plant, it was estimated that on the initial introduction of this material at a time when the boilers were all consistently foaming, the water level in the boilers fell, on an average, three feet. In several cases it was shown that there was so little water actually in the boilers in question that the fires had to be drawn to avoid the possible danger of explosion which would follow.

In this connection it might be stated that, combining precipitation outside with an antifoam treatment inside, boilers can use even the poorest water with a fair degree of satisfaction.

Organic acids, free or in combination, also have a distinct effect in controlling foaming, and there are many cases where they are more effective than the type of treatment already discussed. Sometimes the composition of the water indicates that coagulation alone will take care of the foaming tendency, and in such case the coagulant must be carefully selected to avoid hardening, or making the original supply more corrosive. Frequently, a water which shows no indication whatever will foam, and then operating conditions, possibly contaminated returns, or boiler construction must be investigated. Uneven load, forced boilers, and careless attention can be followed by unexpected difficulties along this line, and often these can be corrected and the boilers operated safely without the otherwise necessary treatment.

Foaming is a trouble which it is impossible to control permanently in some cases, owing to the fact that inorganic concentration is faster than the treatment. Nevertheless, the use of a properly adjusted preparation to control foaming will almost invariably, even with indifferent attention, extend operating periods without trouble two or three times beyond what might previously have been the custom.

Aside from indicating what has been done and what can be done, the discussion of interior treatment is a difficult one. In many cases results are being obtained for which the real reason, or theory, is still uncertain, and one of the greatest handicaps is the difficulty of even approximating boiler conditions for research in a laboratory. Experimental work at atmospheric pressure is misleading, as well as work on one available supply only.

Interior treatment, properly applied, calls for an enormous amount of data, experience, and imagination. Knowledge of the chemical composition of the supply or supplies in use represents only one of the necessary factors to be considered, and internal treatment, while flexible and easy of application, will not give the best results unless based upon thorough knowledge of each individual case.

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[4] Clark and Gage, "Studies of the Relative Corrosion of Metal Pipes by Waters Especially before and after Purification," 42nd Annual Report, Mass. State Board of Health, **1911**.

[5] Cushman and Gardner, "Corrosion and Preservation of Iron and Steel," p. 100.

Disregard of this need for careful study of each case has resulted in the present lack of consideration of this whole field by the scientists who might otherwise be working toward efficiency in the industrial world of power production. Probably more plants are operating with the assistance of some treatment or compound than with all the other types of water purification combined. Such a fact should stimulate research into the underlying theories involved. Unfortunately, it has not, probably because, while intelligent introduction of adjusted treatment can produce results of the highest type, this field is infested with a type of material which borders so closely upon the mysterious, impossible, and unscrupulous as to place it in the same category as the patent medicine in its particular field.

Boiler Compounds

The widespread use of inadequate or unfit boiler compounds is no doubt due to the fact that the salesmen of boiler compounds do not, as a rule, come in contact with the purchasing departments. Rather they visit the tired, discouraged, and sometimes not over-educated boiler operator, who would give a great deal if some of his boiler-room troubles could be overcome. That of scale formation and scale removal is one which bothers him the most frequently.

The many varieties of compounds which are offered in this way vary all the way from preparations containing 98.5 to 99 per cent of water to others carrying 96 to 98 per cent of insoluble siliceous material. For these materials various claims have been put forth, playing upon the hope as well as the credulity of the engineer, or his ignorance of scientific facts, and it is the purpose of this paper to call attention to the types of unscrupulous compounds or some of the methods used to advertise them.

Metal Treatment Type—At the present time probably one of the most common types of preparations is that of the so-called metal treatment which we will call "A."

This material is invariably of the same or similar composition; in other words, it is always a solution of silicate of soda in water, the greatest variety of dyes and chemicals being used to color and disguise the individual compound. All colors of the rainbow are used—even fluorescein, in one case—to give a two-colored product.

The claims all read about the same:

> Boiler Metal Treatment "A" does not treat the water.
> Its action is mechanical, not chemical.
> When introduced into the boiler it immediately enters every pore and crevice in the scale and literally elbows it from the metal by its expansive quality, which is about 20 diameters.

In another booklet covering Metal Treatment "B" is a story, and in this story occurs the following statement:

> That soft lime and sulfate crust that I used to be fighting all the time is porous and has little heat cracks in it. I put this stuff in. The stuff warms up and heads straight for the hot iron in the tubes and shell. It seems to work right through the pores of the scale and when it gets next to the hot metal the stuff begins to swell like a "poisoned pup" and pries the scale off.

With regard to Metal Treatment "C:"

> Remember this metal treatment does not treat the water; it has to insinuate itself through the cracks in the scale all over the boiler surface.

To a chemist this is a pretty clear fake. Silicate of soda is applied as a solution of a soluble alkali salt in water, and when added to any water the solution becomes more dilute, rather than acting as a gum-shoe artist. In the breaking down of the sodium silicate, the alkali (Na_2O) acts like a reduced quantity of caustic soda with the coagulating properties of the free silicic acid added.

Silicate of soda in its proper place in water treatment has a very definite advantage, but to dodge the necessity of water examination and chemical adjustment by ignoring the boiler water, and to argue as in the three quotations above is to take the first step away from the legitimate use of this chemical and place it in the class of fakes.

This type of compound was brought to the attention of the Government several years ago, when it was operating the railroads, and a test was made, covering a period of several months, to determine to what extent the claims as to mechanical action, scale prevention, corrosion prevention, etc., were borne out in practice. A portion of a sentence from the Government's conclusion, in a bulletin issued by the U. S. Railroad Administration, August 29, 1919, is quoted:

> In view of the facts that *none* of the claims advanced in favor of this preparation have been substantiated, and that the results obtained from the test were negative, in so far as any beneficial results were concerned, it is recommended that the use of this product * * * be *prohibited.*

Insoluble Type—Leaving the metal treatment, possibly the next most interesting type to consider would be the "DD" compound. This preparation appears in several forms, with arguments especially interesting and amusing. This type of preparation is almost entirely insoluble in water. As one bulletin says:

> It is a nonvolatile and neutral combination of insoluble earthy salts.

Another bulletin says:

> The material is a combination of nonsoluble powders which are also nonvolatile.

One eminent chemist says:

> It is a dry powder and therefore you are selling 100 per cent material.

Analysis shows this type of material to be either tricalcium phosphate, talc, aluminium phosphate, or some similar insoluble compound.

As to its action, the theory in one bulletin is most amusing:

> Now the theory is this: In the case when scaling water is used and when "DD" is *not* used, the instant that water is transformed into steam the various salts held in solution are transformed into gases, and after flying apart seek to readjust themselves in combination, and look for an affinity or some other salt to amalgamate with. In so doing certain salts, part of which become gas, seek an oxide of iron and oxide of alumina salt or gas. Not finding this in the water and finding it in the steel and iron of the boiler sheets and tubes, it fastens to the sheets and tubes and pulls therefrom such oxide of iron and oxide of alumina that it craves, forming what is commonly known as scale, and leaving holes commonly called pitting. "DD" material furnishes to the water these required salts and the detrimental salts or gases amalgamate with, or eat them instead of the tubes and sheets. In other words, "DD" material is a "food."

In another article advertising the material recommended by the eminent eastern chemist, comparing compound with "DD," there appears something as follows:

> "Compounds" depend largely upon tannates, caustic (or sal) soda, and other like ingredients to do the work. These various acid ingredients work behind the scale, often attacking the metal * * *. The action is too severe, for the scale breaks up in large, flint-like chunks.

Regarding the use of the material the following is quoted:

> This powder is put into the boiler and is carried in rapid circulation to every part of it, bringing the scale down in soft particles. It catches up the oil, so that when the boiler is blown most of the impurities are blown out in the form of a soft sludge. It is possible with the naked eye to distinguish the various elements forming this sludge.

The truth of the matter is that nothing whatever can be expected of a chemical nature from this material. Where it has given results—and it does give results in isolated cases—it has probably been because the insoluble inert material, by mixing with the scale-forming salts which are constantly crystallizing in the boiler, may prevent the compact formation of an all-crystalline scale, thereby rendering its removal with a turbine somewhat less difficult. However, it is a thoroughly good insulating ingredient, and it can do no more than increase the bulk of the scale in which it is incorporated, and, unless the scale does come off for some reason or other, it must of necessity increase its insulating properties.

With this particular type of compound must be classed graphite. This material is what its name indicates, nothing more than commercial graphite. Very frequently some additional geographical term precedes graphite, evidently to increase the value of the material. The same claims are made for graphite as are made for all boiler compounds, and frequently following its use conditions develop which seem to indicate some possible efficiency. However, in an article on boiler compounds appearing in the *Journal of the American Society of Naval Engineers* in 1911, this material is classed under a special heading of "Dangerous Compounds," owing to its distinct corrosive action on the metal. Iron is very definitely electropositive to graphite. This results in the solution of the iron without any action on the graphite, and it is possible that this corrosive action is responsible for the scale removal which frequently follows the introduction of this material. As the article just referred to says:

> Graphite is a scale remover for the same reason that hydrochloric acid is. That is, it corrodes the metal underneath the scale and frees the scale from the metallic surfaces.

Obviously, being insoluble in water, it can have no other effect than a possible mechanical action in keeping apart or interfering with the crystallization of other deposited impurities into a compact scale. It will, however, add itself to the bulk of scale formed, retaining at all times its electronegative effect to the iron as long as the boiler is in operation.

Possibly, the next type of material would be the so-called "X" liquid treatment. This is a sort of homeopathic remedy and contains more water than anything else. It is named usually with interesting foreign scientific names, and its introduction is frequently preceded by a newspaper article (advertisement). For instance, in a New York paper some years ago appeared a special dispatch from Vera Cruz regarding a remarkable discovery by a young Spaniard after much study and experimenting, ending with the statement that the discovery is patented in "seventeen different countries." The analysis of a sample of this material reaching this laboratory showed 98.5 per cent of water. The solution was slightly acid and a faint test for tannin was detected. There seemed to be some gelatinous material present and little or nothing of any value could be detected.

Another preparation was heralded by a booklet explaining the remarkable properties of a colloidal jelly which was embodied in this solution. The analysis showed 88.5 per cent of water, 6 per cent of soda ash, and 6 per cent of a gelatinous material like agar. On standing in the laboratory the material soured rapidly and fermented.

Newspaper articles almost invariably credit the discovery of this material and similar preparations to some point in Mexico or Central America.

It stands to reason that, used in small quantities in the boiler, no possible improvement could be expected. Furthermore, the expense would not permit a larger dosage, as the material just referred to is quoted at about $1.25 a gallon. Granting some colloidal action from the 6 per cent, or less, of organic material, this would only apply to an infinitesimal portion of the scale-forming impurities carried into the average boiler.

Before leaving this "X" type, the writer recalls a preparation of several years ago. The advertising matter pertaining contained the picture of a very exuberant goat, and the preparation, upon analysis, turned out to be a diluted, blue-black, iron-tannin ink, there being about 0.75 per cent of tannate of iron with a little chrome alum and over 98 per cent of water.

These two types of compound, all insoluble and mostly all water, represent the extreme cases of fraudulent compounds. The materials present could have no value under the very best of conditions, and their cost has no relationship whatever to their value. There is a large intermediate class, as well, some of which, under certain conditions and if intelligently used, might give results, but in most cases, where used hit or miss, the same material in the same quantity with all waters, the results cannot help but be discouraging and tend to upset any faith in the intelligent internal use of chemicals for boiler treatment.

RESULTS OF LABORATORY ANALYSIS—This laboratory, since the first of the year, has analyzed eighty-six entirely different boiler compounds which represent the average of what is now being marketed. Twenty-two represent the metal treatment type and three the insoluble type. In the all-water group are included such compounds as contained 75 per cent or more of water, and of this particular type fourteen samples were received. These fourteen samples might be classified as follows: those containing soda ash as the other ingredient totaled seven, from 10 to 13 per cent soda ash being present, the balance being usually coloring matter, as a rule organic extract, although amorphous carbon was used in one case; those containing organic matter only, usually a very dilute tannin extract, totaled five; a suspension of graphite in water, containing nearly 25 per cent of graphite and 75 per cent of water; and one containing 4 per cent of organic matter and 5 per cent of trisodium phosphate. These preparations are manifestly worthless and yet in no case were they marketed for less than 15 cents per pound.

The other extreme is the preparation containing mostly soda ash. Soda ash, being cheap and reacting quickly with sulfate of lime, has always been a favorite with the compound quack. It can be bought with or without water of crystallization, and costs very nearly the same in either condition. Of the samples analyzed, nine of the eighty-six were of this character, containing 80 per cent or more of soda ash, the difference being coloring material, sometimes with a little caustic soda, and the ordinary impurities of a commercial product.

These preparations are all guaranteed to prevent scale and eliminate corrosion under all conditions. In one case a company handling an almost pure soda ash, save for a slight color, advertised that this compound was a by-product of a very intricate method of organic manufacture, and later advertising matter states they have been compelled to greatly enlarge their plant to cover several additional acres, owing to the demand for this remarkable product.

In addition to the straight soda ash is the preparation which masquerades as soda ash but which is not. In other words, the washing soda preparation containing 45 to 52 per cent of water of crystallization, the balance being carbonate of soda with natural manufacturing impurities. Here for the same price one gets but half such efficiency as might be had from soda ash. Trisodium phosphate, commonly used many years ago, does not seem to be so generally marketed as it was, although two samples of this material were analyzed. While this is an efficient chemical if properly used, its 50 per cent water of crystallization must not be overlooked, nor the fact that its reactive value is less than that of soda ash.

Next worthy of consideration comes the compound supplied in brick form. In this form the intention is evidently to give the impression of solidity. In this case advantage is taken of the fact that carbonate of soda can exist in a dry (?) form, both with water of crystallization and without. Consequently, by bringing together soda ash and tannin extract and allowing a portion of the materials to become pretty well mixed, the resultant compound can be left alone with perfect confidence that, when cold, its physical condition will be that of a hard, brown-colored brick, in which the original soda ash exists partly as such and partly as the carbonate of soda containing more water of crystallization.

A great many samples of this sort of material come into the laboratory. Since the first of the year out of fourteen samples received, all but one contained soda ash as the reacting chemical and tannin extract. The soda ash content ran all the way from 34.5 to 75 per cent, the water content varying from 35 per cent down to about 14 per cent. The balance was usually organic matter, although some of the bricks contained graphite. In addition, one contained 17 per cent of sulfate of soda; one, 30 per cent of sulfate of soda; one, 4 per cent of metallic mercury; two, less than 10 per cent of sodium phosphate; one, castor oil; and one contained silicate of soda, trisodium phosphate, and caustic soda in addition to the soda ash and organic matter.

One of the most typical, which we will call "OU," was described in a booklet containing some of the most remarkable arguments ever advanced in handling a boiler compound. Quotations from this booklet are illuminating:

> The secret process by which "OU" compound is made lies with the inventor, and that secret will not be detected by any chemist or school chemistry.
>
> Chemists are like all other human beings. They know a great deal, but they do not know everything. They know what they have been taught in school, but the teachers of the school in which they received their educations learned everything they knew from their predecessors and from experiments with what had already been invented.
>
> When different kinds of chemicals, which are required to neutralize minerals in water, are mixed together, they will neutralize each other and therefore become ineffective and will not neutralize the minerals which are contained in water, and for that reason those who have attempted to make a boiler compound from the knowledge they received in chemical schools have made a failure, and for that reason also, we were compelled, in order to make good boiler compounds, to invent and create chemicals or certain kinds of material which are not known to chemistry.

One of the most popular liquid preparations contains from 17 to 19 per cent of caustic soda in water colored brown. This is sold in huge drums, and even tank cars, at a price all out of proportion to its caustic content. Its popularity is largely due to a personal financial rebate made the purchaser.

Paste preparations appear on the market containing sometimes 85 per cent of water with enough starch to thoroughly gelatinize the mixture and make it seem very hard, heavy, and honest.

Ordinary common salt is a frequent adulterant. Two samples analyzed showed 41 and 45 per cent of common table salt. Powdered mixtures sometimes contain, in addition to soda ash and other chemicals already referred to, sodium sulfate. Probably this is to keep the preparation dry.

In connection with all these preparations, it must be remembered that each one is a specific recommended for virtually all sorts and conditions of water.

OTHER "TREATMENTS"—One or two other methods of treatment, fortunately not now in general use, must not be overlooked. Several years ago, through Germany and Great Britain came an equipment known as "Luminator." *Chemical Abstracts* at that time summarized the theory and operation as follows:

> Water allowed to run down a bright corrugated Al plate induces an electric current, which causes ionization of the scale-forming salts so that they become amorphous. The apparatus must be exposed to light and air and preferably to a north or south light for best results. Water treated by this process should be used within seven days.

Strange to say, this equipment was actually sold and installed in a great many American plants, one large eastern railroad putting up a unit 15 to 20 feet in height. Needless to say, the flow of the water down the corrugated plate in the bright sunlight was never followed by anything more than profanity.

Another type along the same line is entirely mechanical. It is:

> Done without the introduction of chemicals within the water or boiler. * * * It is a machine of an extremely sensitive alloy of *pure metals*. This machine is attached to the feed water line of a boiler, or battery of boilers, and all of the water must pass through the machine before entering the boiler. The action of the machine causes a liberation of fine particles of the metal to enter the water through the abrasion of its parts. These fine particles at once attack the scale forming minerals and salts, thereby preventing them from *cementing themselves together or to the iron of the boiler*.
>
> The principle involved is very simple and is readily understood. * * * The iron of a boiler is a metal, made up for *durability*. "Our machine" is a very pure, soft metal. * * * It has a greater affinity for the scale-forming elements, which will naturally attach themselves to the pure and more sensitive metal rather than to the iron of the boiler.
>
> No analysis is required, as "our machine" treats all waters.

The equipment consisted of a metal chamber containing a number of white metal balls, seven or more, around which the water flowed. Chemical analysis indicated the balls to be nothing more than Babbitt metal, practically all of the same general composition. Needless to say, these arguments are not borne out. The water does not do what the claims indicate, and mental depression only follows the use of this material.

THE TRUTH ABOUT BOILER COMPOUNDS

A consistent and earnest reading of the patents on compounds registered at the various patent offices is amusing. There is no specific that can handle all conditions. It is only the ignorant demand for the millennium that makes possible the life of such preparations. A moment's thought should be enough to convince one of the impossibility of getting something for almost nothing, although very frequently a great deal is paid for trouble.

The fact should never be overlooked that these various chemicals, when used, all do something when brought in contact with the salts naturally present in the water. In certain cases some of these combinations unquestionably would represent the proper material for use. Many of them, used with intelligence, would produce satisfaction. In no case, however, is there shown any effort on the part of the manufacturer to adjust chemical treatment to any individual water, and the advertising matter and arguments show such ignorance of chemical facts as to suggest the impossibility of the average compound manufacturer even knowing what he is doing. The firms which are treating water thoughtfully by this method do not give their materials fancy names, nor call them compounds or specifics. They refer to them as "treatment," and recommend a treatment with discretion. The success and magnitude of the results obtained through internal treatment indicate the efficiency of a properly recommended and manufactured chemical treatment used inside the steam boiler.

The United States Government in its *Water Supply Papers* has been in the habit of indicating this fact, but always with the qualification that only when intelligently recommended and compounded should confidence be placed in the boiler compound.

The Properties of Activated Carbon Which Determine Its Industrial Applications[1]

By N. K. Chaney, Arthur B. Ray, and Ancel St. John

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In 1919 the senior author published[1,] a preliminary account of investigations, eventuating in the processes for making gas-mask carbon, which were adopted and exclusively employed by the U. S. Chemical Warfare Service during the war. This paper summarized the conceptions as to the nature of active carbon and the theories of activation which had proved successful as a working hypothesis in directing this work. Since then the investigation of both the technical and theoretical phases of carbon activation has been continued in this laboratory, and the scope of the work broadened to cover the general problem of the physical nature and interrelationships of the various forms of carbon. New lines of attack have been employed, including the development of special methods and technic for utilizing X-ray crystallographic analysis.*

I PRINCIPLES OF ACTIVATION

The general theory of carbon activation set forth in the 1919 paper may be summarized as follows:

1—In addition to the recognized forms of graphite and diamond, two forms of carbon possessing distinctive physical properties are postulated: (1) to explain the observation that free carbon liberated from its compounds below a certain critical temperature range (in which decomposition occurs) was either active or capable of yielding active carbon, while free carbon liberated at higher temperatures (approximately 600° to 700° C.) was both inactive and incapable of activation by any known means; (2) to account for the unique differences in chemical reactivity and adsorptive power of the high and low temperature forms of carbon after treatment by activating processes.

2—The formation in all primary carbons, such as low temperature chars and cokes, of a peculiarly stable adsorption complex between the active carbon and the residual hydrocarbons was postulated for the following reasons: (1) this would logically result from the unique adsorptive power predicated of active carbon; (2) it accounted for the saturated and relatively nonadsorptive properties of ordinary chars; (3) it accounted for the fact that carbon deposited at low temperatures from carbon monoxide and other nonhydrocarbon compounds was highly active and required no activation; (4) the persistence of residual hydrocarbons in chars heated far above the normal decomposition temperature of the hydrocarbons was explained as a result of the protective mechanism of such adsorption; (5) finally, it was in harmony with all known facts and processes of activation, and directly suggested the most effective principle of all—namely, that of selective chemical attack upon the adsorption complex by means of controlled oxidation.

Thus, the features which distinguished the original disclosures of the Chaney processes of carbon activation were (1) a clear-cut differentiation for the first time between the inherently activatable and the inactivatable forms of carbon, and recognition of the fact that the controlling factor in determining whether carbon would assume the activatable or the inactivatable form was the temperature at which the elementary carbon was liberated from its compounds; (2) the concept of the activatable forms of carbon (so-called "primary" carbon) as consisting of a uniquely stable complex of active carbon and adsorbed hydrocarbons, and the activation process as consisting of the separation of these adsorbed hydrocarbons from the active carbon by means of a selective chemical reaction carried to a definite quantitative conclusion.

Because of their deficiency at precisely these points, the vague disclosures of the prior art proved of no practical value to the allied chemists. None adequately defined the conditions essential to the production of the activatable forms of carbon in quantity under commercial conditions, nor taught that the activating environment should be employed in a well-defined manner to achieve a specific chemical reaction. Chemists of the French Army Service actually experimented with a process employing "high temperature steam" said to have been used in Russia, and definitely rejected it as giving an unsatisfactory product.

To illustrate further the vital and complementary character of these principles in the development of successful methods for the large-scale production of highly active carbon, the following is cited:

Early in 1918 the U. S. A. Chemical Warfare Service was under heavy pressure to find a substitute for the inadequate supply of coconut and similar shell carbon. It was already employing the Chaney processes of selective oxidation, by both air and steam methods as applied to properly prepared coconut and wood charcoals. Acting upon information from the National Carbon Company's laboratories that anthracite was capable of activation, their engineers secured a retort from a gas company in Springfield, Mass., filled it half full of 8 to 10-mesh anthracite coal of a selected grade, introduced a steam pipe at the bottom of the retort, raised the temperature to 900° C., and tried to activate the anthracite. The outcome was a complete failure. Samples of the anthracite from the retort when later returned to the laboratory were found to be not only inactive, but absolutely incapable of activation even under ideal laboratory conditions; whereas the original raw anthracite was readily activated under precisely the same conditions. In the light of these two postulates the explanation was obvious enough. The heating of the retort had been carried on in such a manner that large sections of the anthracite had reached a high temperature while other portions were still undergoing active distillation at lower temperatures. The hydrocarbon vapors distilling from the low temperature sections had then passed through and been "cracked" upon the more highly heated anthracite particles at temperatures above the critical decomposition temperature range, and had been deposited in the pores of the anthracite as inactive carbon. As this deposit of inactive carbon was highly resistant to oxidation, the application of selective oxidation processes to the gas-treated anthracite merely burned away the active carbon (together with the hydrocarbons) and left the inactive form and the ash as the end product. Equipped with this information the engineer then employed an inclined retort, and by properly controlling the heating, the steam concentrations, and the circulation of hydrocarbon vapors, worked out a routine method which permitted the manufacture of a moderately good gas-mask carbon from anthracite in ton lots. By using this carbon (Batchite) mixed with the better grade shell carbon in ratios of about 1 part in 3, a serious shortage of gas-mask carbon was averted.

This example is cited because it so clearly illustrates the inadequacy of certain earlier statements as to the heating of carbon at high temperatures in the presence of steam, and shows why such references led to no fruitful results. In addition, however, to the practical coördination of the several principles underlying these two postulates as to the general nature of activation, the Chaney disclosures involve a third principle which is specific to the preparation of the highest types of gas-adsorbent carbons. This principle arises from the fact that military uses and most industrial applications involving the adsorption of gases and vapors place a heavy premium upon the maximum of adsorptive capacity per unit volume of adsorbent. As a result, it may be shown that there must exist a definite critical density or porosity of adsorbent, corresponding to its maximum capacity per unit of volume. Other things being equal, any departure from this critical density in either direction impairs the potential adsorptive capacity of the carbon. The reasoning is obvious. If the porosity approaches zero the available exposure of active carbon becomes negligible. A space entirely filled with carbon atoms has no room for adsorbable molecules. On the other hand, as the porosity approaches 100 per cent the mass of active carbon per unit of volume approaches zero, and its adsorptive capacity falls off accordingly. Between these two extremes there is a certain density or porosity in which the maximum mass of active carbon is most effectively exposed. It has been experimentally determined for steam-activated shell carbon that this critical apparent density is about 0.4 (for 8 to 10-mesh granules), or that the desired porosity of the individual granule should be 66 per cent.

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[1] Presented before the 15th Semiannual Meeting of the American Institute of Chemical Engineers, Wilmington, Del., June 20 to 23, 1923.

* Numbers in text refer to bibliography at end of article.

The actual value of this critical density was determined by observing the density at and below which the adsorptive power of the carbon per unit of mass became constant. As a matter of observation all highly activated carbons having a density of less than 0.4 (for 8 to 10-mesh granules) tend to approach a substantially constant adsorptive capacity per unit weight of carbon, which means that their capacity per unit volume then becomes a simple function of their density.

This is illustrated by the data in the following tables taken from reports by Chaney in 1918 to the Chemical Warfare Service.

TABLE I—CAPACITY OF TYPICAL CHARCOALS FOR ABSORBING CHLOROPICRIN WHEN COMPLETELY ACTUATED

SOURCE	AD	S'	$S'/10AD$	SW
Coconut............	0.430	955	222	0.76
Babassu nut........	0.330	770	233	0.82
Cedar..............	0.103	240	234	0.78
Sycamore...........	0.097	227	234	0.79

The capacity S' is the number of minutes service on C. W. S. standard tube test. SW is the adsorptive capacity expressed as weight of chloropicrin absorbed by 1 gram of carbon under the same test conditions. AD is the apparent density of 8 to 10-mesh carbon granules.

As shown in Column 3, the ratio of the service time or gas capacity to the apparent density for fully activated chars of less than 0.4 density is practically constant. Column 4 shows the same thing—i. e., per unit weight of carbon the capacity of all fully activated chars is approximately constant, if the densities are less than the critical density. In this particular series the coconut sample is somewhat above the critical density, which accounts for its slight deviation from the constant in Column 3. On the other hand, all coconut chars in which the selective oxidation has been substantially completed, but which are above 0.41 in apparent density, were found to obey the following empirical formula:

$$K = \frac{BP}{(1 - P)\ S} \qquad (1)$$

where BP = porosity of the carbon granules, P = total porosity, and S = service capacity. In other words, the service (expressed either in minutes or service time or in weight of chloropicrin adsorbed per cubic centimeter of carbon) is a function of the porosity. The values of K were experimentally determined from the following, which is another form of Equation 1:

$$K = \frac{RD \times BP}{AD \times S} \qquad (2)$$

where RD = real density, and AD = apparent density of 8 to 10-mesh carbon.

TABLE II—ADSORBING CAPACITY OF STEAM-ACTIVATED COCONUT CHARCOALS

Sample (1)	Series (2)	S' (Observed) Minutes (3)	BP (4)	RD (5)	AD (6)	$\frac{RD \times BP}{AD}$ (7)	S^a (8)	K (9)
Unactivated		0	0.253	1.56	0.715	0.51	0.0000	∞
1	D	6	0.382	1.66	0.626	0.98	0.0027	370.0
2	E	112	0.350	1.63	0.634	0.90	0.0381	23.7
3	F	250	0.417	1.66	0.580	1.19	0.0832	14.3
4	D	387	0.532	1.87	0.525	1.90	0.1305	14.5
5	E	430	0.510	1.86	0.548	1.62	0.1449	11.3
6	C	464	0.504	1.98	0.590	1.69	0.1565	10.8
7	H	515	0.511	1.93	0.567	1.74	0.1740	10.0
8	E	525	0.510	1.90	0.563	1.71	0.1760	9.7
9	B	532	0.522	2.04	0.585	1.82	0.1805	10.1
10	E	540	0.537	1.96	0.544	1.93	0.1818	10.6
11	D	545	0.525	1.95	0.555	1.85	0.1830	10.1
12	D	566	0.537	1.90	0.529	1.93	0.1905	10.1
13	E	577	0.600	2.02	0.497	2.38	0.1943	12.7
14	C	580	0.535	2.04	0.572	1.90	0.1957	9.7
15	B	600	0.540	2.08	0.576	1.94	0.2020	9.7
16	C	605	0.505	2.02	0.600	1.70	0.2040	8.3
17	A	610	0.545	2.04	0.558	2.00	0.2060	9.7
18	B	615	0.574	2.10	0.539	2.23	0.2077	10.7
19	B	654	0.584	2.08	0.521	2.31	0.2207	10.5
20	A	662	0.575	2.09	0.534	2.25	0.2240	10.0
21	H	687	0.515	2.03	0.591	1.77	0.2317	8.1
22	A	700	0.584	2.15	0.540	2.31	0.2354	9.9
23	H	760	0.545	2.02	0.553	1.98	0.2555	7.9
24	H	775	0.567	2.02	0.535	2.11	0.2615	8.0
25	C	800	0.584	2.08	0.522	2.31	0.2680	8.7
26	F	805	0.617	2.11	0.484	2.70	0.2713	9.9
27	F	825	0.617	2.11	0.484	2.70	0.2780	9.7
28	F	845	0.612	2.11	0.488	2.65	0.2855	9.3
29	F	900	0.654	2.17	0.452	3.13	0.3033	10.2
30	H	955	0.665	2.14	0.432	3.28	0.3207	10.2

S = Grams of chloropicrin absorbed per cubic centimeter of charcoal.
S' = Number of minutes standard C. W. S. test.

Table II gives data upon a series of steam-activated coconut charcoals from eight independent sources (samples of common source indicated by same series letter between which the degree of oxidation is the only variable). These samples are arranged in the order of their service capacity shown in Column 3. A well-defined break appears with increasing activity at a service capacity of about 450 minutes. The initial activation period is marked by rapidly falling values of K. The second stage, covering a service range of from 450 to 950 minutes, or a chloropicrin capacity of from 0.16 to 0.32 gram per cubic centimeter of carbon, exhibits a well-defined tendency for K to approach a constant value. Considering the necessarily approximate nature of the experimental values and the extraneous variables in the preparation of the carbon samples, the agreement in the values of K is unmistakably significant. This table reveals two of the three characteristic stages occurring in the progressive oxidation of carbon:

1—The stage of selective or differential oxidation, in which the chemical character of the carbon is undergoing rapid change by the elimination of associated hydrocarbons. In this stage the adsorptive power increases at a rate out of all proportion to the increase in porosity, as shown by the rapidly falling value of K.

2—The stage of limited oxidation, which commences after the chemical changes on the exposed carbon surfaces have been substantially completed. That the sole function of this continued oxidation is to increase the porosity and available surface is shown by the fact that K becomes constant and therefore that the increase in capacity is derived principally from physical changes in the carbon which are mathematically expressible as a function of its porosity. In the latter part of Table II this second stage is shown approaching the limit set by the critical density of 0.4. Unfortunately, the third stage is not represented, as the samples selected for this series did not happen to pass through the critical density, but Table I serves the same purpose, showing the final phase below the critical density where the capacity per unit mass displays a constant value over a fourfold range in densities.

Further direct evidence confirming the existence of these three characteristic phases of selective and limited oxidation has been presented by one of the authors recently,[33] in which it was shown that the first stage of activation is characterized by a very rapid decrease in hydrogen content corresponding to the selective removal of the hydrocarbons. In the period of limited oxidation following, the hydrogen content becomes practically constant, and the retentivity at first continues to increase with increasing porosity corresponding to the second stage, and finally becomes constant as the third stage is reached.

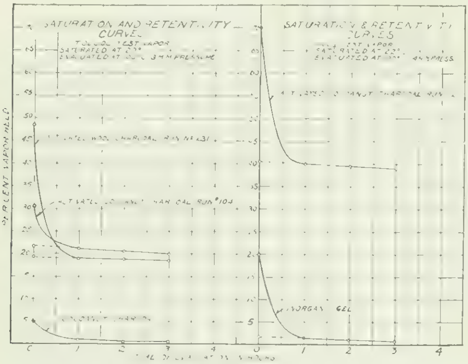

FIG. 1

The best gas-adsorbent carbon can never be made directly from wood charcoals. With the exception of a few hard woods, of which the supply is negligible, the wood chars are too low in density even before activation. Only by pulverizing low density wood charcoals and briquetting them to denser chars can they be made to compare with dense nut chars. On the other hand, coconut shell chars as obtained immediately after distillation are too high in density. Therefore, after the differential oxidation is substantially completed the oxidation process must be continued through a definite secondary stage, until the critical apparent density is reached, if the maximum adsorptive capacity is to be attained.

In commercial practice the rapidly mounting costs of continued oxidation sometimes make it advisable to stop short of the ideal or theoretical density for certain industrial uses. In other cases high capacity is so vitally important to the efficiency of the process that the higher cost of carbon becomes a secondary matter. This is also true of carbon for military purposes. The engineer must determine in each case to what extent space and high capacity per unit of volume are vital factors, and be prepared to pay the necessary premium for his requirements.

THEORY OF ALPHA AND BETA MODIFICATIONS

Turning back for a moment to the postulates of the original theory, discussion of these since their publication has centered principally around the statement that the active and inactive forms of carbons constituted two distinct modifications. It is, of course, possible to argue endlessly over matters of definition. The term "modification" was purposely selected as sufficiently broad to permit more exact definition on further evidence. To quote the language of the paper, "It would be premature to assert that these two forms of carbon are true allotropic modifications. It is not yet established that both forms are amorphous. * * * This much is established, the two forms are characteristically distinct and easily differentiated both by their properties and conditions of formation." However, in provisionally suggesting the terms "alpha" and "beta" carbon for the active and inactive forms, expression was given to a belief that future work would disclose some tangible differences in molecular aggregation or arrangement corresponding to the unique difference in properties. It was considered extremely probable that alpha carbon would prove to be almost, if not completely, amorphous and of a loose, open structure—possibly having a large proportion of free valences by reason of this loosely packed arrangement; whereas beta carbon was expected to prove more akin to graphite, having a more definitely close-packed or crystalline structure. In this laboratory the latter was sometimes referred to as "amorphous graphite." In view of this it is interesting to note that Professor Briggs, of Edinburgh, after taking exception to this classification, proceeds to ascribe the difference between the active and inactive forms to a difference in the degree of polymerization.[2]

In view of the widespread interest and speculation on this subject, the writers are perhaps warranted in pointing out the trend of their present investigations, and in indicating the nature of certain tentative conclusions which they have drawn therefrom. While these conclusions are now being subjected to a rigorous examination before being put out in final form, they serve to indicate the basis upon which it is hoped to obtain a final answer as to the existence and nature of the structural differences between alpha and beta carbon as defined by the terms "active" carbon and "inactive" carbon.

Briefly stated, the X-ray crystallographic and chemical evidence thus far obtained indicates that all forms of carbon (the diamond excepted) fall into two main classes, the graphitic and the pseudo-graphitic.

All normal graphites, natural and artificial, are sharply crystalline and have a common characteristic X-ray pattern. (All the so-called "amorphous" graphites are completely crystalline; so also is graphitic acid which has a perfectly definite physical and chemical structure. The confusion caused by the close resemblances of these two forms of carbon is responsible for the thesis so elaborately developed by Kohlschutter[3] that graphite is not a definite chemical individual.) They all yield graphitic acid by the Brodie reaction.

The pseudo-graphites are also definitely crystalline, but have a distinctly modified X-ray pattern, and do not readily yield graphitic acid; at least, they are much less susceptible and may be readily distinguished from the normal graphites which are readily converted. This fact permits a chemical separation of the two forms. The proportions of these two forms in mixtures can also be identified by the X-ray to within 5 or 10 per cent. The pseudo-graphites also have an electrical resistance about five times higher than the graphites, the comparisons being based upon finely divided samples of each. Perhaps the simplest evidence of the stability and individuality of these two crystalline forms of carbon is the fact that a graphite-psuedo-graphite thermocouple junction gives definite and reproducible thermoelectric potentials over temperatures ranging from 1500° to 2400° C., the potential in the neighborhood of 1700° C. being about 15 millivolts.

All other forms of carbon are converted into one of these two ultimate crystalline forms when heated above graphitizing temperatures. The types of free carbon from which active carbon is most easily derived—namely, carbohydrate and cellulosic chars, wood and nut charcoals, lampblacks, carbon blacks, filter blacks, etc.—yield pseudo-graphite. Therefore, in accordance with the previous nomenclature, all the less highly polymerized forms of carbon which yield pseudo-graphite on heating have been termed "alpha carbon." Correspondingly, all forms of carbon which yield normal graphite on heating may be designated as "beta carbon."

In the 1919 paper the inactivable forms of carbon—i. e., carbons set free from their compounds at high temperatures

—were defined as beta carbon. These forms now satisfy the new beta carbon classification by yielding normal graphite on heating.

On this basis active carbon appears to be simply a pure form of alpha carbon possessing fundamentally the elements of the pseudo-graphitic crystalline structure, whereas inactive carbon is beta carbon belonging to the graphitic type of structure. This apparently simple relationship is clouded somewhat by the fact that certain low-temperature cokes and the coals yield beta carbon predominantly on heating and yet, as the writers have shown, are capable of reasonable activation. Either they must abandon the thesis that unique adsorptive properties are inherent in the special structure of alpha carbon, and conclude that both alpha and beta forms may be active if in a sufficiently degraded state of polymerization, or they must conclude that the coals and pitch cokes referred to above contain a certain percentage of alpha carbon mixed with beta carbon. One possibility is that the free carbon in coal is largely alpha and that the beta carbon is formed during calcination from the hydrocarbons in it having a high temperature of decomposition. In this case they would expect a previously activated anthracite coal to yield pseudo-graphite predominantly, because the hydrocarbons ordinarily giving rise to beta carbon on heating would have been chemically removed by oxidation. The experimental work along these lines is not yet sufficiently advanced to say whether coals already contain beta carbon in considerable quantity or whether it appears later in the calcining stages.

However, other evidences of the relationships between the four forms of carbon—alpha, beta, pseudo-graphite, and normal graphite—lead to the suspicion that the special adsorptive powers of active carbon will be found to be specific to the alpha form. Starting with graphite, the writers have made the other three forms by way of graphitic acid in a manner which indicates that alpha carbon must have a simpler unit of crystal structure than beta. By a partial breaking down of the structure of the graphite crystal they obtain beta carbon which goes back to graphite on heating. If, however, the graphite crystal is more completely disintegrated, alpha carbon is obtained which then goes to pseudo-graphite on heating. This clearly suggests that there is some element of complexity in the beta carbon grouping which determines its crystallization in the graphitic rather than the pseudo-graphitic form, and consequently that beta carbon is probably more complex than alpha carbon.

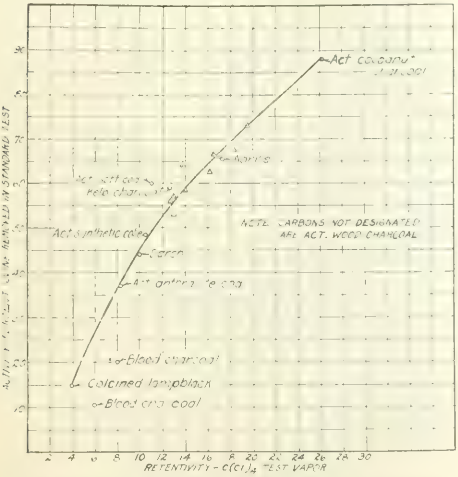

Fig. 2—Relationship between "Activity" and "Retentivity" of Various Types of Activated Carbons
All carbons acid-extracted, thoroughly washed and dried before testing.

Furthermore, beta carbon is found to be merely colloidal graphite and may be directly obtained by mechanically breaking down the graphite crystals to fragments of colloidal dimensions. This actually occurs in the preparation of Aquadag, which the X-ray shows to be highly polymerized beta carbon and which is made from fully crystalline graphite by a process of grinding and deflocculation. Colloidal graphite such as Aquadag exhibits no extraordinary adsorptive powers beyond those characteristic of all materials in so minute a state of subdivision. So far as the writers know neither it nor similar forms can be activated. It therefore seems reasonable to assume that the special adsorptive properties of active carbon are peculiar to the simpler structure of alpha carbon.

The transition from alpha carbon to pseudo-graphite with increasing temperature can be observed by the changes in X-ray patterns in a manner analogous to the transition of beta carbon to graphite. This crystallization causes the alpha carbon to lose its special activity. Pseudo-graphite, even when made from highly active carbon, is not appreciably more active than graphite.

If the observations and relationships just indicated are substantiated by subsequent work, the nature of the active and inactive modifications of carbon will be definitely established along the lines suggested in the original paper.

II—FUNDAMENTAL CRITERIA OF ACTIVATION AND ADSORPTIVE CAPACITY

This discussion relates to a phase of the commercial utilization of adsorptive materials of great importance—namely, the question of quantitative criteria of useful adsorptive capacity. To make real headway it must be possible to market a standardized product permitting of definite engineering specifications.

The first essential step is a method of defining and measuring adsorptive capacity in terms that are of quantitative significance to the user and at the same time are sufficiently simple and accurate for manufacturing control. The first such criteria to come into general use in this country were the tube tests developed and used by the Chemical Warfare Service as specifications for gas-mask carbon.[4]

Air containing a known concentration of toxic vapor, such as chloropicrin, was passed at a constant rate into a tube of fixed diameter containing a 10-cm. layer of carbon of a definite fineness. The capacity of the carbon was then expressed by the number of minutes to the break point—i. e., to the point where a detectable trace of vapor appeared in the effluent air. The weight of gas adsorbed at the break point was also determined directly. For reasons which will be apparent, the break point on such a test is affected by many factors which bear no relation to the intrinsic character of the carbon itself, as, for example, the concentrations of the vapor, the rate of flow of the air, the fineness or mesh limits of the carbon, etc.

As the quality of the adsorbent carbon was improved, it became necessary to accelerate the tube tests by using higher concentrations and faster rates of flow. While such accelerated tests served to give relative values for manufacturing control at any given plant, they gave badly distorted values when applied to adsorbent carbons of different origin and type such as the American and German carbons. Therefore, not even for military uses were the accelerated tests authoritative.

Attempts were made to substitute a saturation test in which the absorbed gas was weighed after the carbon had come to equilibrium with a definite concentration of the gas at a definite temperature. In a C. W. S. report in 1919, one of the authors showed that in general a constant difference existed between the weight of gas taken up by the carbon on any given saturation test and the corresponding tube test. This was explained as follows:

> The break point on the tube test corresponds to the point where the rate of adsorption falls below the rate at which the gas was being passed through the tube. This critical point appears to be reached when the residual unsaturated capacity of the carbon drops to a constant minimum value, this constant value depending upon the particular factors of the tube test. Thus, the two tests are not directly proportional, but the saturation values are proportional to the sum of the tube test values plus a constant, which is characteristic of the test. The saturation test, while free of certain extraneous factors, such as geometrical shape of container, gas velocity, etc., is extremely sensitive to gas concentration, and fails to show more than partial correspondence with the significant differences in behavior of various kinds of carbon, either for military or industrial purposes.

The reasons for this lack of correspondence lie in the dual character of the sorptive phenomena exhibited by carbon, as cited in the earlier paper.[1] In his series of C. W. S. reports, Chaney showed that if pure air was passed over the carbon, either after the break point on the tube test or after the saturation test, the losses of absorbed gas were first very high and then fell to a gradual and almost negligibly low rate—one too slight to be detectable by the usual methods of determining the break point. Plotted logarithmically, the periods of rapid and slow weight loss appeared as two intersecting straight lines, indicating a more or less abrupt discontinuity between the two rates of loss. The weight of adsorbed gas corresponding to the period of extremely slow weight loss was termed the "retentivity" of the carbon. The retentivity values for a series of typical carbons were found to bear no fixed relationship to the saturation values, but to show a most significent correspondence to certain other properties of the carbons, such as their value for vapor recovery from low concentrations, their power to adsorb substances in true solution such as iodine, and their relative value for different kinds of toxic gas removal. The conclusions drawn were that the retentivity values corresponded most nearly to what was termed the "specific" adsorptive capacity—i. e., associated with the chemical properties of the active carbon—and that the excess of more easily removable gas or vapor was held by capillary forces associated with the physical or microscopic structure of the carbon. A further reason for believing that the specific adsorptive power represented specific polar forces was the observation that water, for example, showed a zero retentivity value, being practically completely removed by the passage of dry air at room temperature. The high retentivity values for hydrocarbon derivatives were thus directly associated with the chemical nature of the adsorbed vapors, and not merely with their physical properties such as the boiling points. The industrial significance of this will be discussed later in connection with comparative data on silica gel.

The method of determining the retentivity by passing air over the saturated carbon at room temperatures was one requiring several hundred hours for completion, and consequently, means of accelerating the test were sought. As finally developed to a routine procedure in this laboratory, the method consists in first saturating the dried and evacuated carbon with toluene or carbon tetrachloride at 22° C., the weight of absorbed gas after equilibrium is established giving the saturation value. The carbon is then evacuated to 2 mm. of mercury at 100° C., weighings being taken each half-hour. When the last three weighings lie on a straight line, the intercept of this line extended to the y-axis is taken as the retentivity value. Fig. 1 illustrates the type of curves obtained in hundreds of determinations. The difference between the saturation value and the retentivity value has been called the capillary value of the carbon. The ratio of capillary and retentivity values may vary enormously, and therefore the saturation and retentivity curve serves to define the sorptive characteristics of any carbon with a definiteness and completeness unapproached by any other method.

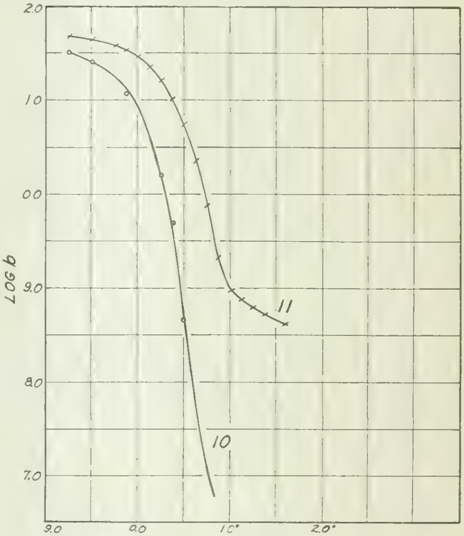

FIG. 3—RELATIVE EVACUATING POWER OF TWO ACTIVATED CHARS FOR AIR

It is true that the retentivity values thus obtained are also purely relative, the absolute weights of retained gas depending upon the chemical nature of the vapor selected, the temperature at which it is removed, and upon the degree of vacuum employed. On the other hand, the values thus obtained are the first to show any broad relationships and permit of any basic generalizations as to various types of adsorptive phenomena, and hence must be accepted as corresponding in some real way to a fundamental property of the carbon. The exactness of this correspondence with the iodine adsorption number or the carbon, for example (Fig. 2), has permitted the substitution of the latter and simpler test, whenever the retentivity value alone is required, as is usually the case for carbons of known type where the ratio of capillarity to retentivity has been previously determined. It is also evident that when this ratio is known for a given type of commercial carbon, the saturation values alone can be used as a commercial test, without serious error. To compare or define an unknown carbon, however, the complete determination both of the saturation value and of either the retentivity or the iodine number is necessary. The latter value has been termed the "activity" of the carbon, and is obtained by determining the amount of iodine which 1 gram of dried 200-mesh carbon will absorb from 50 cc. of 0.2 N iodine-potassium iodide solution. The mixture is agitated for 3 minutes, filtered, and the first runnings of the filtrate are discarded. The iodine concentration of an aliquot portion of the filtrate is determined by titration. Highly activated carbons will remove about 90 per cent of the iodine.

Other criteria of carbon activation have been proposed, notably the methods of Lemon,[5] who has measured the relative vacuum produced by the adsorption of air or nitrogen at liquid air temperatures. The pressure curves thus obtained (Fig. 3) are related to the retentivity, or, as Briggs[6] defines it, to the "prehensility" of the carbon, but both the technical difficulties of the method and the greater difficulty of expressing the values in convenient quantitative terms make it of theoretical interest only.

III—GENERAL PROCESSES OF CARBON ACTIVATION

The previous discussion has shown that according to the theory of the writers any process of releasing carbon from its compounds at sufficiently low temperatures in the absence of hydrocarbons or other strongly adsorbed substances should yield highly active carbon directly.

This has been accomplished in several ways—for example, by employing the reaction $2CO = C + CO_2$, which can be brought about at 300° C. in the presence of an iron oxide catalyst (first suggested in the present connection by Patterson at the American University in 1918), and by the action of sodium[7] or mercury[8] on carbon tetrachloride. Such methods are of purely theoretical interest, as the resulting carbon lacks the necessary mechanical properties for use even as a decolorizing carbon, as will be more fully discussed in a later section.

The requisite physical structure for commercial uses can be obtained only in suitably prepared chars, cokes, or coals, which have been termed "primary carbon." These all require activation—that is, the adsorption complex characteristic of the primary carbon must be broken up and the hydrocarbon constituents eliminated. The following methods have been employed or suggested:

High Temperature Calcination—The difficulties of this method on a commercial scale are evident from the theory. The stabilization of the hydrocarbons by adsorption usually raises their final decomposition temperature above the critical temperature range, and inactive carbon is formed. By selecting chars naturally having a low decomposition point and conducting the operations with great care a limited degree of activation can be effected. However, the method does not permit control of the resulting porosity of the carbon granules, and is only effective on chars of very low density, which means low structural strength and low capacity per unit volume of adsorbent. The wood charcoals employed for gas masks by the British and French were chiefly prepared by this method.

Carbonization with Mineral Additions—The carbonaceous materials may be impregnated with a variety of metallic salts or oxides before carbonization. These seem to be effective in preventing the formation of the adsorption complex of hydrocarbons or in causing the decomposition of the adsorbed hydrocarbons. The removal of mineral matter provides an exceedingly porous structure with capillary pockets of molecular dimensions. Such carbons possess a relatively high capillary capacity, but exhibit the specific adsorptive characteristics of active carbon only to a limited degree. The German gas-mask carbon was prepared by this method, the wood being impregnated with zinc chloride, calcined, and then the zinc dissolved out by hydrochloric acid. This type of process is familiar in the more common methods of preparing certain decolorizing carbons. Sometimes the mineral naturally occurs in the vegetable fibers, as in the case of "Carbrox" made from rice hulls.

Use of Solvents—It has been proposed to dissolve the hydrocarbons out of the primary carbon by special solvents, such as selenium oxychloride.[9] Such methods, apart from their expense, do not appear commercial even for war emergencies, as they do not afford means of controlling the porosity or density of the final product. The problem of getting rid of the solvent is also a serious one.

Processes Involving the Principles of Differential and Limited Oxidation—Of universal applicability to all primary carbons and of the widest flexibility, both as to the manner of employment and as to the variety and quality of the resulting product, are the processes involving what have been termed "differential" and "limited" oxidation. While these may be carried out by either wet or dry methods, in their preferred forms the oxidizing agents are gases, such as air, steam, carbon dioxide, chlorine, etc. The principle of such selective chemical attack depends upon the slightly greater susceptibility to oxidation of the hydrocarbon constituents of the adsorption complex than of the active carbon itself. By a proper adjustment of the oxidizing environment as to temperature and concentration, the adsorbed hydrocarbons may be eliminated from the active carbon far more effectively and economically than by any other processes hitherto employed, and in the same environment the formation of inactive carbon may be reduced to a minimum. The Chemical Warfare Service employed both air and steam activation on a large scale. The product obtained by air is inherently inferior to the best steam-activated products, chiefly because the difficulty of nicely controlling the temperature and rate of an exothermic reaction is much greater than is the control of an endothermic one. Too harsh an oxidizing attack destroys both active carbon and hydrocarbons simultaneously; consequently, nothing is accomplished by it except a general increase in porosity.

The quality of activated carbon, therefore, depends upon the skill with which the manufacturer is able to control the

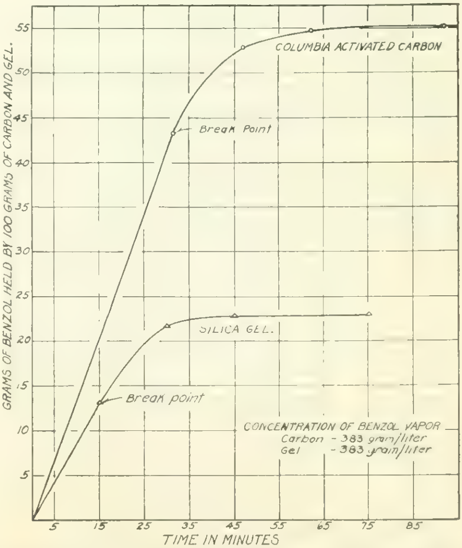

Fig. 4—Sorption of Benzene Vapor from Dry Air by Activated Carbon and Silica Gel

Equal volumes (30 cc.) of 8 to 14 mesh carbon and gel compared. Air-benzene mixture passed at rate of 500 cc. per min., temperature 25° C.

oxidation environment, as well as upon the preliminary preparation of the char.

NOTE—The essential features of the steam-activating processes were worked out by an Austrian, Ostrejko, a year or more prior to the American disclosures. For military reasons his patents were withheld from issue in Austria until after the war, although curiously enough he obtained an issue from the British Patent Office in the spring of 1918.[10] His disclosures, therefore, were, unknown to the allied chemists until after the American processes were in operation, and were apparently not developed or employed by either Austria or Germany during the war.

IV—ADSORPTION OF GASES AND VAPORS BY CARBON AND SILICA GEL

The three essential characteristics of a gas-adsorbent carbon are good mechanical strength, a close approximation to a definite optimum density or porosity, and high intrinsic activity. The necessity for mechanical strength to avoid crushing, packing, and dusting in containers or towers through which large volumes of gas must be passed at high velocities is obvious.

The fact that the efficiency both of military and industrial gas-adsorbing vessels is rated upon the size of the container, rather than upon the weight of the adsorbent filler, automatically determines the ideal porosity of the adsorbent in the manner discussed in Section I.

Section II has also shown why the most significant criterion of the adsorptive capacity of carbon is its specific capacity as defined by the retentivity for certain adsorbed gases, or by the equivalent values of the iodine adsorption from solution, designated as the "activity." The industrial significance of the activity values will be further developed in connection with the question of preferential or selective sorption, a quality of solid adsorbents which is made strikingly apparent by the retentivity method. In respect to this property, active carbon and silica gel are found to be diametrically opposed with respect to their relative adsorption of water and hydrocarbon derivatives.

The fact has already been mentioned that if the retentivity of carbon were defined by its power of retaining water vapor, instead of toluene, for example, the retentivity would be zero. In a stream of dry air, carbon gives up its water at room temperatures. Applying the same criteria to silica gel, its specific adsorptive power, while much less marked than that of carbon, is definitely selective for water. In fact, all the water cannot be expelled from the gel without breaking down the physical structure or the granules, and this makes the selection of a basis for defining the water retentivity a little difficult. If, however, the gel, dried at 200° C. (and already containing about 3 per cent of water), is saturated with water and the additional water retained at 100° C. is determined, this is found to be about 2.5 per cent, whereas the toluene retentivity of the gel treated in the same manner is but 1.5 per cent—that is, the ratio is 5 to 3 in favor of the water. If the original water content is included, the ratio of water to toluene is 4 to 1.

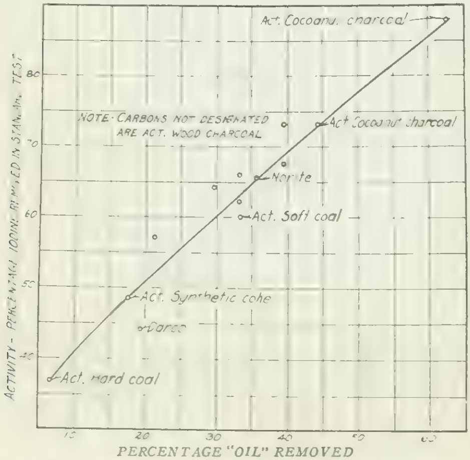

FIG 5—RELATIONSHIP BETWEEN ACTIVITY AND ALCOHOL PURIFYING POWER OF VARIOUS TYPES OF ACTIVATED CARBON

All carbons pulverized to pass 200-mesh screen, acid-extracted, thoroughly washed, and dried before testing.

Crude alcohol containing objectionable oil treated with 5 per cent carbon in the cold. Oil determination made by comparing turbidities on dilution by means of nephelometer.

That this selectivity of adsorption is a very practical reality is readily demonstrated by the simple experiment of shaking up a mixture of water and benzene with activated carbon and silica gel, respectively. The carbon will adsorb the benzene, and if enough benzene is present to saturate the carbon the water will be completely rejected. The silica gel will take up the water and reject the benzene. These facts prove beyond question that any theory of adsorption which disregards the chemical nature of the adsorbent and adsorbed substances is incomplete from a theoretical point of view and inadequate from a practical standpoint. As a matter of fact, even a capillary theory of adsorption must recognize the predetermining influence of specific chemical factors, inasmuch as capillary phenomena may exhibit certain sharply contrasting aspects depending upon whether the capillaries are wet by the liquid or not. Such differences in the wetting action reveal the operation of specific chemical or polar forces, which are not explicable on any mathematical concept as simple as relative capillary diameters.[32] This statement is made, not in order to minimize the significance of the role played by capillary structure in the dispersion of solid adsorbents, nor to deny the value of statistical studies of capillary and pore volumes in the case of any given absorbent, but to avoid a fictitiously simple classification of all adsorbents and adsorptive phenomena on the basis of mechanical structure.

TABLE III—SORPTIVE CAPACITY OF ACTIVATED CARBONS AND SILICA GEL
(Saturation in pure vapor at 25° C. Retentivity at 100° C. and 3 mm. Hg pressure)

SUBSTANCE	APPARENT DENSITY 8 to 14 Mesh	SORPTIVE CAPACITY EXPRESSED AS GRAMS CCl_4 HELD BY 100 GRAMS SORBENT		
		Total	Capillary	Specific
Activated carbon A	0.465	110.9	80.9	30.0
Activated carbon B	0.500	103.8	75.3	28.5
Activated carbon C	0.542	95.7	68.7	27.0
Activated carbon D	0.560	79.5	51.5	28.0
Silica gel A	0.720	19.8	17.8	2.0
Silica gel B	0.700	39.2	37.7	1.5
Sil-o-cel	...	12.3	10.3	2.0

In Table III are characteristic data on the sorptive capacities of typical samples of activated carbon, silica gel, and sil-o-cel—both their specific capacities or retentivities under similar conditions and their total saturation capacities. Attention is first called to the fact that the sorption by silica gel and sil-o-cel for carbon tetrachloride, for example, is almost wholly of the capillary type, their retentivity for this class of substances being practically negligible under the conditions of the test. The industrial significance of these differences in retentive power is shown by Fig. 4, dealing with the relative recovery of benzene from dry air by carbon and silica gel. The most significant points on these curves are the break points representing the end of the period of complete sorption of benzene. These results are typical of the superiority exhibited by activated carbon over silica gel for all organic vapors and solvents. The conditions above are those most favorable to the silica gel, because the benzene-air mixture was moisture-free. The industrial significance of a solvent-preferring *vs.* a water-preferring adsorbent is illustrated by the data in Table IV showing the relative recoveries of benzene from dry and moist air. The efficiency of the carbon is slightly impaired, but the silica gel becomes entirely valueless.

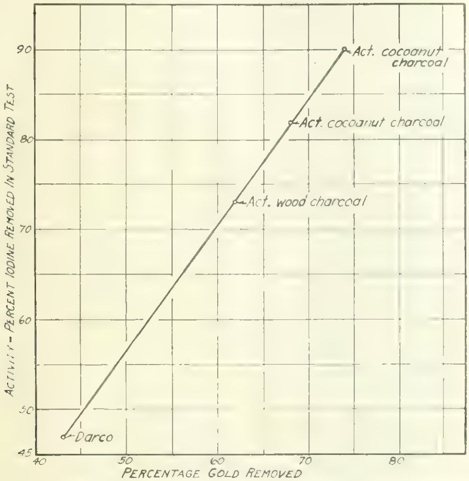

FIG. 6—REMOVAL OF GOLD FROM GOLD CHLORIDE SOLUTION BY ACTIVATED CARBON OF DIFFERENT ACTIVITIES

All carbons pulverized to pass 200 mesh, acid-extracted, thoroughly washed and dried before testing. Equal weights of carbons agitated with gold chloride solution at 25° C. for 10 minutes.

It is this selective adsorption of water which destroys the military value of silica gel, ferric oxide gel, and similar hydrophilic adsorbents, and the lack of it that makes carbon of unique and irreplaceable value.

TABLE IV—PREFERENTIAL SORPTION OF BENZENE AND WATER VAPOR BY ACTIVATED CARBON AND SILICA GEL

SORBENT	Weight of Sorbent G.	AIR	BREAK POINT Time Min.	BREAK POINT Benzene Held Per cent	SATURATION Time Min.	SATURATION Benzene Held Per cent	Concentration of Benzene G./Liter
Carbon B	33	Dry	230	27.8	420	..	0.0133
Carbon B	33	Dry	207	31.9	420	34.9	0 017
Gel B	50	Dry	62	5.0	420	12.0	0.0134
Gel B	50	Dry	68	5.6	..	..	0.0137
Carbon B	33	Moist	166	21 2	..	..	0.0142
Carbon B	33	Moist	162	20.9	420	27.3	0.0142
Gel B	50	Moist	29	2.4	420	0.0	0.0135
Gel B	50	Moist	28	3.0	420	0.0	0.0178

The amount of benzene adsorbed from moist air was determined by removing it from the sorbent by steam.

Equal volumes of 8 to 14-mesh carbon and gel B used.

Dry air containing benzene or air containing approximately equal parts by weight of water vapor and benzene passed at rate of 3000 cc. per minute.

REMOVAL OF VOLATILE SUBSTANCES FROM CARBON

In certain quarters it has been argued that the high retentivity of carbon for the more common volatile solvents and chemicals was not an advantage but a handicap in industrial recoveries because of the supposed difficulties of removing the adsorbed materials from the carbon. As a matter of fact, for most substances which it is desired to recover, this difficulty does not exist. While retentivity of carbon for many hydrocarbon derivatives is marked in comparison with that of other adsorbents, and while the relative retentivity values under arbitrarily selected conditions have been found to afford one of the most significant indexes of the characteristic sorption properties of carbon, nevertheless, the retentive power rapidly diminishes at critical temperatures characteristic for each substance, and the more volatile chemical vapors are removed from carbon as readily as from silica gel at moderate temperature elevations, especially when aided by steam distillation or vacuum. Comparative data are given in Table V.

TABLE V—REMOVAL OF SORBED VAPORS FROM ACTIVATED CARBON AND SILICA GEL BY HEATING AT 150° C.

(Saturated materials exposed in a thin layer in a ventilated oven and heated for 1 hour at 150° C.)

SOLVENT	Percentage Solvent Held at Saturation by Carbon B	Percentage Solvent Held at Saturation by Gel B	Percentage Solvent Retained at 150° C. Carbon	Percentage Solvent Retained at 150° C. Gel
Methanol	50.0	20.0	1.21	1.50
Ethanol	50.0	20.0	1.05	1.54
Isopropanol	50.0	20.0	1.15	1.75
Ethyl acetate	57.5	25.0	4.87	2.84
Acetone	51.0	20.0	2.93	1.20
Acetic acid	70.0	25.0	2.23	.75

In the case of materials immiscible with water, steam or hot water provides the simplest and most rapid method of introducing the required heat. Moreover, the drying of the carbon after the removal of the adsorbed materials by steam or water is in many cases unnecessary, owing to the nonselective sorption of the latter and its easy displacement by preferentially adsorbed vapors. This possible omission of the drying step constitutes a unique economic advantage in certain industrial sorption cycles employing carbon. Substances miscible in water require indirect heating or rectification.

TYPICAL COMMERCIAL APPLICATIONS OF GAS-ADSORBENT TYPES OF ACTIVATED CARBON

There are five general fields in which the gas-adsorbent carbons have marked technical possibilities:

1—RECOVERY OF GASES, SOLVENTS, AND VAPORS IN DILUTE CONCENTRATIONS

(*a*) Recovery of gasoline from natural gas;[11,12] recovery of solvents such as petroleum ethers, benzene, sulfuric ether, ethyl acetate, alcohol, etc., from the air.[13]
Recovery of acetone, butanol, ethanol, etc., from waste gases passing out of fermenting vats;[14] removal of sulfur compounds,[15] as well as recovery of benzene and light oil from illuminating gas;[16] recovery of oxides of nitrogen, sulfur dioxide, etc.

(*b*) Abatement of objectionable stenches and odors—e. g., from rendering plants, etc.;[17] purification of air in submarines; deodorizing of confined spaces in refrigerating rooms, etc.

(*c*) Military, firemen's, and industrial protective masks.[18]

2—PURIFICATION OF GASES

(*a*) Refining of helium.[19]

(*b*) Purification of gases—e. g., to make carbon dioxide from fermenting vats available for carbonated waters; purifying hydrogen and nickel carbonyl[20] for hydrogenation purposes; purifying ammonia[21] before its catalytic oxidation, etc.

3—CATALYSIS OF GAS REACTIONS

(*a*) Decomposition or oxidation of hydrogen sulfide to yield free sulfur.[15]

(*b*) Decomposition of phosphine (in ammonia and acetylene purifications).[22]

(*c*) Oxidation of nitric oxides[23] by air (500-fold accelerations have been obtained in comparison with ordinary tower processes).

(*d*) Chlorination of hydrocarbons,[24] also of carbon monoxide in the manufacture of phosgene.

(*e*) As a general means of facilitating reactions between a gas and a liquid by passing the two countercurrently through a column of granular carbon.[25] Applicable in bleaching, in sterilizing water and other liquids with chlorine, in the oxidation of drying and semidrying oils, in the decomposition or oxidation of mineral oils for conversion into fatty acids, etc. The usefulness of active carbon in catalytic reactions may be widely extended through its impregnation with various metals, oxides, and salts.

4—STORAGE OF COMPRESSED GASES—It has been shown that at corresponding pressures more of certain fixed gases can be stored in a cylinder containing highly active carbon than in the same cylinder with no carbon present.[26] This is due to partial liquefaction of the gases by adsorption at high pressures, and is exhibited only by adsorbents possessing a high retentivity.

5—Evacuation of Vessels—This is allied to (4) above, the production of high vacua being a function of the retentivity of the carbon. In these uses carbon is again sharply differentiated from silica gel, which has a low evacuating power or "prehensility."[6] The carbon may be used:

(*a*) For cheaply and simply evacuating commercial heat-insulating containers, and

(*b*) In various forms of special apparatus where a sensitive method of regulating the vacuum or of maintaining it in the presence of slight gaseous decompositions is desired.

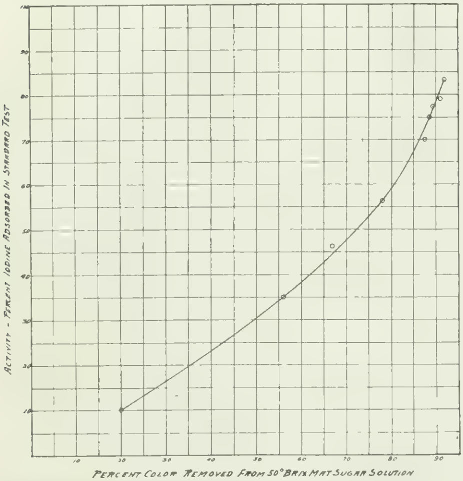

Fig. 7—Relationship between Activity and Decolorizing Power of Activated Carbons for Sugar Solution

All carbons of approximately same apparent density, low ash content, and pulverized to pass 200 mesh. Five per cent carbon on basis of solids present used in decolorizing tests.

V—ADSORPTION FROM LIQUORS AND SOLUTIONS

An examination of the voluminous literature upon decolorization of sugar and other solutions by carbon suffices to indicate a considerable degree of confusion and incoherence in the technology of decolorizing carbons. Theoretical discussions of the inherent properties and behaviors of such carbons have notably failed to produce any broad generalizations which could adequately satisfy the known facts. In the study of decolorizing problems in this laboratory, one of the authors has employed to unique advantage the systematic variations in carbon activity and structure made possible by precise control of the activating processes, and has utilized the special methods of evaluating active carbon described in Section II. He has found that the various phenomena relating to decolorizing and adsorptive efficiencies can be adequately correlated and the behavior of any decolorizing carbon fairly accurately predicted under diverse circumstances on the basis of the following very simple generalizations:

1—The adsorptive power of any carbon for substances in liquids is directly proportional to its activity (as defined by the retentive capacity of the carbon for gases), provided the units of the substances to be adsorbed are small enough or the porosity or subdivision of the carbon is great enough to permit unobstructed access to the active carbon.

Two special cases exist:

(*a*) If the dispersion of the carbon—i. e., its porosity or fineness—passes certain limits, its adsorptive power becomes completely defined by its activity, independently of the dimensions of the particles adsorbed.

(*b*) If the dispersion of a carbon is limited, its adsorptive power for larger particles of colloidal dimensions becomes a function, not only of the activity of the carbon, but also of its apparent density and of its fineness.

2—The adsorptive power of carbon for particles bearing an electrical charge is diminished if the carbon bears a charge of like sign and increased if the carbon is oppositely charged.

In discussing the first generalization, reference should be made to Fig. 2 showing the correspondence between the retentivity of active carbon for a specifically adsorbed vapor such as toluene and its capacity for removing iodine from solution. This illustrates the parallelism between the specific adsorptive power of carbon for gases and for substances in solution when the adsorbed molecules are of equivalent dimensions.

Wherever the substances to be adsorbed are of molecular dimensions, we may therefore expect the retentivity or the activity, as represented by the iodine number, to be a true index of the performance of any carbon. Fig. 5, showing the removal of a soluble oil from alcohol by carbons of widely varying densities, and Fig. 6, showing that the removal of gold from solution is proportional to the retentivity, illustrate how this expectation is realized.

Considering the adsorption of particles of colloidal dimensions, in accordance with the first generalization it is found that all carbons of equivalent porosity or apparent density possess adsorptive capacities for colloidal particles which are directly proportional to their activity, as shown in Fig. 7. If, however, carbons of various apparent densities are considered, no regular correspondence is found between the density or the activity separately and the decolorizing power of the carbon. This is shown in Table VI, where a variety of technical and special carbons are arranged in the order of diminishing decolorizing power for a standard sugar solution (Column 4).

Table VI—Comparative Data Regarding Various Activated Carbons

(All carbons pulverized to pass 200 mesh, acid-extracted, thoroughly washed, and dried before testing.)

Nature of Carbon	*AD* (200 to 270-Mesh) (1)	Activity (2)	Ratio of Activity to AD (3)	Color Removed from Sugar Solution Per cent (4)	Ash Content Per cent (5)
Activated wood charcoal	0.382	73.0	191	91.0	1.44
Activated coconut charcoal	0 548	95.0	173	90.0	0.83
Activated wood charcoal	0.426	64.0	150	89.4	2.30
Kelpchar	0.216	59.0	273	88.2	12.96
Norit	0.393	65.6	167	88.2	3.38
Activated soft coal	0.413	60.0	145	86.9	23.75
Activated wood charcoal	0.472	67.5	143	86.8	2.97
	0.419	53.1	127	86.1	0.75
	0.528	65.9	125	86.1	2.15
	0.376	46.5	123	85.3	1.32
	0.471	56.0	118	85.2	0.88
	0.503	58.5	116	85.4	4.03
Darco	0.470	44.0	93.6	85.7	36.63
Activated wood charcoal	0.570	57.0	100	83.3	1.74
	0.647	62.5	96	76.5	1.04
Activated coconut charcoal	0.766	72.9	93	62.3	2.14
Activated synthetic coke	0.714	48.5	68	33.3	9.19

The order of the densities in Column 1 and of the activities in Column 2 does not diminish with any corresponding regularity. If, however, as in Column 3, we take the ratio of the values in Column 2 to those in Column 1, we find the values of this ratio lie on a fairly smooth curve when plotted against decolorizing power. This is shown in Fig. 8. In other words, the adsorptive power of carbon for particles of colloidal dimensions is a mathematical function of the ratio of its activity to its apparent density, fineness being constant.

The second generalization—namely, that a given carbon will be most effective as an adsorbent if it carries an electrical charge opposite in sign to that carried by the particle to be adsorbed—will be accepted as axiomatic.[27,28,29] The justification for this statement is the fact that it accounts for the only variables in the performance of decolorizing carbons which are not adequately covered in the first generalization. Active carbon may be neutral, or may readily become positively or negatively charged by the adsorption of hydrogen or hydroxyl ions from solution. This explains why the decolorizing power of all carbons for sugar solutions is increased when the solution is acid. The coloring matter consists mainly of negatively charged colloids. On the other hand, the color particles in cottonseed oil are positively charged, and its acidification decreases the decolorizing power of the carbon. The carbon may be caused to assume the desired electrical charge prior to its introduction into any given solution or liquid. The effect of such treatment on adsorptive power is shown in Fig. 9, and is readily demonstrated by the effect upon the adsorption of ionized coloring matters such as Ponceau Red, which is positive, and Methylene Blue, the colored ion of which is negative.

The somewhat anomalous reverses in the order of decolorizing power observed between different carbons when used for certain oils and in aqueous solution will find complete explanation when the effect of the electrical charge is considered. The fact that a given carbon is electrically charged, for example, does not influence its adsorptive capacity when it happens to be reacting toward neutral particles, but becomes of decided moment when it is employed to adsorb particles which carry an electrical charge.

Since the ability to assume such electrical charges is common to all forms of active carbon, the differences in adsorptive power caused merely by differences in electrical charge on the carbon are not fundamental in estimating the intrinsic character of the carbon. Such effects, nevertheless, have been a fruitful source of confusion in comparative evaluation of many special decolorizing carbons. The generalizations above permit the selection of tests which are criteria of the fundamental properties of the carbon and are not merely peculiar to the special characteristics of a given liquid or adsorbable substance. They also facilitate the intelligent specialization of the properties of the carbon for specific uses by appropriate selection of the raw materials and modifications of the activation processes.

The fallacious character of such generalizations as those attempting to relate decolorizing value to nitrogen content has been adequately treated by others.[30] A recent observation[31] attempting to relate the decolorizing power of carbon to the hydrogen content of the carbon is a special case, valid only for carbons made by the same process from the same raw material over a limited range of conditions. Its significance depends upon the fact that activation involves the elimination of hydrocarbons by one means or another, and therefore increase in activity goes hand in hand with a diminished hydrogen content.

Selection of Decolorizing Carbons

It will be evident from the preceding section that the physical requirements of a carbon for adsorption from solutions and liquids are much more varied than is the case for gas adsorbent carbons. The preferred physical form of the carbon will depend upon such factors as the size of the particles to be adsorbed, the viscosity of the liquid, the nature of the methods required for recovery of the adsorbed material from the carbon and revivification of the latter, and the engineering methods employed for handling the carbon, whether by the tower system, or by filtration or centrifuging the carbon from the liquid.

For removing particles of molecular dimensions from liquids of high mobility, a dense granular gas carbon will be as effective as the finer or more porous forms of equal activation. If the carbon is easily revivified *in situ* by moderate heating, steam, or solvents, the granular type with tower system may be distinctly indicated. As the size of the adsorbed particles approaches colloidal dimensions, increasing dispersion of the carbon is necessary. If pulverulent forms of carbon are used, resort must be had to filter press or similar mechanical systems for handling the carbon. Even for the latter type of carbon, however, the physical structure is of vital importance. If the carbon is devoid of structure or too soft and impalpable, it slimes the filter, or may go into colloidal solution in certain solvents. Therefore, a definite structure is essential to good filtering properties. Carbons made from raw materials lacking in pronounced structural character, such as soft coal, are generally poor in filtering quality.

Dispersion of solid adsorbents can be accomplished in two ways—by increasing the porosity of the particle, and by increasing its fineness. Some forms of decolorizing carbon owe their effectiveness in adsorbing colloidal particles to their extreme fineness, coupled with relatively low porosity and activity. Others of less minute subdivision owe their value to higher porosity of particle and higher intrinsic activity. The latter are superior, not only in filtering qualities, but in their more universal applicability, as they are equally effective for particles of colloidal and molecular dimensions.

The viscosity of the liquid is also a determining factor. The rate of adsorption is dependent upon diffusion velocities. It may be desirable, therefore, to increase the rate of adsorption by raising the temperature, at a sacrifice of total adsorptive capacity. High viscosity in the liquid requires either an increase in the time of contact or in the degree of dispersion of the carbon.

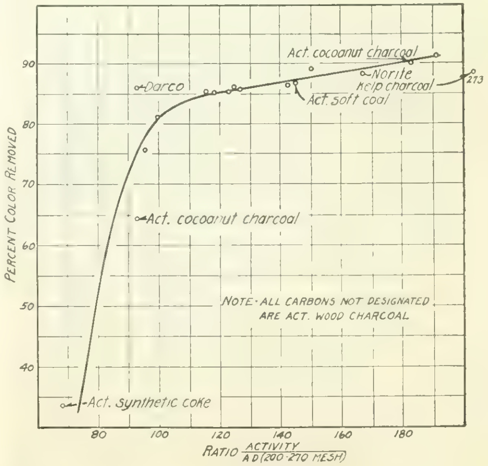

Fig. 8—Relationship between Ratio of Activity to Apparent Density and Sugar Decolorizing Power of Activated Carbons

All carbons pulverized to pass 200-mesh screen, acid-extracted, thoroughly washed and dried before testing. Ten per cent carbon on basis of solids present used in decolorizing a very dark 50° Brix mat sugar solution.

In numerous cases, however, technical success can be achieved only by the use of special types and not all the commercial forms of decolorizing carbon are in any sense technical equivalents. For example, some decolorizing carbons on the market have no prospective value as sugar decolorizers because of their lack of good filtering properties, although possessing properties which fit them for special uses. Where purity, the highest possible activity, and high porosity with good mechanical structure are required, steam-activated wood char is unapproached in quality but at present is also most expensive. The purification of acids is restricted to those carbons which are both free from soluble ash and of high activity. To prepare organic chemicals of the highest purity a high activity is usually essential. In many of the heavier and more viscous liquids, such as glycol, a carbon of excessive fineness and softness goes into colloidal solution and cannot be filtered out. In the treatment of edible oils carbon has an advantage over fuller's earth, since the earthy flavor imparted by the latter is sometimes unpleasing. For water filters at office fountains, etc., a special type of porous block filter can be made. Methods have been developed for preparing bonded blocks of activated carbon of any desired size and porosity. Steel containers of any shape and dimension can be filled with a continuous porous mass of active carbon, eliminating all dusting, packing, or settling, such as may occur with loose granular carbon, and possessing extremely desirable mechanical properties for certain uses.

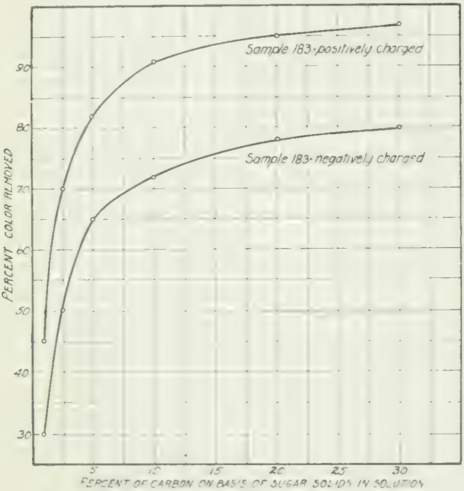

Fig. 9—Effect of Electrical Charge upon the Decolorizing Efficiency of Activated Carbons in 50° Brix Mat Sugar Solution

Carbons pulverized to pass 200 mesh and freed from soluble constituents before testing.

It is further evident that the type of carbon to be selected for a given purpose cannot be considered apart from the development of the appropriate engineering methods for its employment. The high degree to which the mechanical methods of handling bone black have been developed in sugar refining, and the lack of equally well perfected and successful engineering methods for handling finely powdered materials, such as the decolorizing carbons, gives the former its chief competitive advantage. The question of ash removal is not a real factor, because precipitated calcium phosphate is much more effective as an ash remover than is the calcium phosphate in the bone black, just as the best types of activated carbons are more efficient decolorizers than the carbon in bone black. There is no inherent reason why ash removal and decolorization should be combined in a single operation if the two can be more efficiently performed separately. As the technology of the manufacture of decolorizing carbons of any required type nears solution, the extension of their use has largely become an engineering problem.

To recapitulate, mechanical form and structure have been shown to be as significant as the content of active carbon itself in determining the industrial applications of activated carbon. It has been shown that the required densities of the gas-adsorbent types fall within a relatively narrow range, whereas, for employing in liquids, the preferred physical properties may vary from the high densities of the ideal gas adsorbent to the high porosity and subdivision desired of a good sugar decolorizing carbon. The principal reason for this wider range of physical properties required of adsorbents employed in liquids is the enormously wider range in size of particles which the latter type is required to adsorb. The versatility of service expected of this class of carbons can be more clearly visualized by a resumé of a few typical applications.

Industrial Applications for Activated Carbon in Liquids

(1) Making white sugar directly from cane juice; ultimately its use in part or whole in refineries.
(2) Purification of both organic and inorganic acids, such as lactic, citric, acetic, tartaric, phosphoric, etc.
(3) Purification of a great variety of organic liquids—alcohols, acetone, cane, maltose and glucose sirups, glycerol, glycol, etc.
(4) Decolorization of waxes, gelatin, glue, etc.
(5) Removing objectionable colors and flavors from edible oils and fats.
(6) Decolorizing and purifying petroleum oils.
(7) Water-purifying filter, removing tastes, odors, and bacteria.
(8) Recovery of rare metals such as gold from dilute solutions.
(9) Recovery of alkaloids from solution.
(10) Pharmaceutical and medical reagents and preparations.

The technical possibilities of all these uses have been proved on a laboratory scale. Some are in the industrial stage and some depend upon current market conditions or the requisite engineering development for commercial success.

The pharmaceutical and medical applications are for the most part still in the laboratory stages. A few uses have already appeared. The possibilities of a physical and physiologically inert adsorbent of high purity and high adsorbent activity nonselective as to water are so numerous, both as a reagent and for direct therapeutical application, that further developments in this field may be reasonably anticipated.

To meet the requirements of this range of industrial service, the activation of carbon by the Chaney processes of selective oxidation is uniquely adapted, because it possesses the latitude in choice of raw materials and the flexibility of treatment by which any desired combination of physical properties and activation can be secured.

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The Estimation of Pentoses and Pentosans[1]

II—The Determination of Furfural

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Several new volumetric methods for the determination of furfural in dilute aqueous solution were tested out. Iodine in alkaline solution could not be used because the results could not be accurately duplicated. The trials with acid permanganate were also unsuccessful, owing to catalytic reduction of the permanganate by furfural. The use of potassium bromate in acidified furfural solutions containing potassium bromide was eminently successful.

Specific directions are given for obtaining theoretical yields of furfural from pentose materials and for the volumetric determination of this substance in the resulting distillates. Representative results of determinations on pure pentoses and pure furfural are recorded which seem to justify the use of the following theoretical factors for the conversion of potassium bromate used to furfural, pentose, pentosan, or the corresponding methyl derivatives:

FACTORS FOR CONVERTING GRAMS OF $KBrO_3$ USED

	Method of Calculation	Factor	Log
Furfural	$3C_5H_4O_2 . KBrO_3$	1.7254	0.236890
Pentose	$3C_5H_{10}O_5$ $KBrO_3$	2.6961	0.430736
Pentosan	$3C_5H_8O_4$ $KBrO_3$	2.3726	0.375225
Methylfurfural	$3C_6H_6O_2 . KBrO_3$	1.9758	0.295743
Methylpentose	$3C_6H_{12}O_5 \cdot KBrO_3$	2.9481	0.469542
Methylpentosan	$3C_6H_{10}O_4$ $KBrO_3$	2.6244	0.419024
Rhamnose hydrate	$3C_6H_{12}O_5H_2O : KBrO_3$	3.2717	0.514782

FACTORS FOR CONVERTING CUBIC CENTIMETERS OF 0.1 *N* $KBrO_3$ USED

Furfural	0.0027837 × Factor	0.004803	$\bar{3}.681513$
Pentose	0.0027837 × Factor	0.007505	$\bar{3}.875351$
Pentosan	0.0027837 × Factor	0.006605	$\bar{3}.819873$
Methylfurfural	0.0027837 × Factor	0.005500	$\bar{3}.740363$
Methylpentose	0.0027837 × Factor	0.008207	3.914184
Methylpentosan	0.0027837 × Factor	0.007305	$\bar{3}.863620$
Rhamnose hydrate	0.0027837 × Factor	0.009107	$\bar{3}.959375$

MANY reagents have been proposed for the estimation of the furfural obtained from the acid distillation of pentose. The principal ones are reviewed below.

AMMONIA—The earliest method proposed was that of Stone and Tollens (1888),[2] which involved the precipitation of the furfural by ammonia and subsequent weighing of the resulting furfuramide. The method was quite unsatisfactory owing to incomplete precipitation of the furfural [Günther, de Chalmot and Tollens (1891), Stone (1891)].

PHENYLHYDRAZINE—This was proposed by the work of Fischer (1884). Günther and Tollens (1890) and Günther, de Chalmot, and Tollens (1891) titrated furfural with a standardized phenylhydrazine solution using aniline acetate paper as indicator. Stone (1891) used Fehling's solution to determine the end point. Ling and Nanji (1921) precipitated the furfural and determined the excess phenylhydrazine by iodometry. Flint and Tollens (1892) and others have shown that the use of this reagent in volumetric estimations is rather unsatisfactory owing to instability of the solution and the fact that it reacts with levulinic acid arising from hexoses, giving an indefinite end point. Phenylhydrazine was also used as a gravimetric reagent [de Chalmot and Tollens (1891), de Chalmot (1893, 1894)]. Günther, de Chalmot, and Tollens (1891), Flint and Tollens (1892), and Mann, Krüger, and Tollens (1896) undertook comparative studies of all the phenylhydrazine methods, and concluded that the gravimetric method was best. However, the furfural hydrazone was difficult to dry properly and conversion factors had to be determined experimentally. This reagent has also been used in the gaseometric determination of furfural [Gregore and Carpiaux (1898), Menaul and Dowell (1919)].

PYROGALLOL—Hotter (1893) heated acidified furfural solutions with pyrogallol in sealed tubes at 110° C. and weighed the resulting precipitates.

SEMIOXAMIZINE—This was used by Kerp and Unger (1897), who obtained low results with its use. Kreeman and Klein (1917) also used it in their study of the kinetics of the reaction whereby pentoses are transformed into furfural.

PHLOROGLUCINOL—Wheeler and Tollens (1889) first applied phloroglucinol as a color test, and Councler (1894) adapted the test to the gravimetric estimation of furfural. The method was studied by Welbel and Zeisel (1895), Mann, Krüger, and Tollens (1896), Tollens (1902), and Grund (1902). The first of these found that methylfurfural was also precipitated so that methylpentoses could be determined by the same method [Votocek (1897), Widtsoe, and Tollens (1900)]. Kröber (1900, 1901) amplified and perfected the whole pentose procedure and determined by actual experiment the factors and tables for the conversion of various weights of phloroglucinol precipitate into the corresponding weights of arabinose, xylose, pentose, and pentosan. Kröber's results were verified by Kröber, Rimbach, and Tollens (1902, 1902*a*). Mayer and Tollens (1907) then extended the Kröber procedure to include fucose, while Ellett and Tollens (1905) did the same for rhamnose. The latter investigators further found that both methylpentoses and pentoses could be estimated in the same sample by applying Votocek's (1897) observation on the relative solubilities of methylfurfural and furfuralphloroglucide in 95 per cent alcohol at 60° C. Ishida and Tollens (1911) advised the use of a Soxhlet apparatus in the alcoholic extraction, but Schorger (1917) showed that this is less accurate than simple maceration of the precipitate with alcohol. Schorger further claimed that the procedure of Ellett and Tollens gave results which were too high for both pentose and methylpentose. Pinoff (1905) studied the reaction between furfural and phloroglucinol in alcoholic solution. Böddinger and Tollens (1910) proposed shortening the time required for precipitation by heating the solution, but this modification has been criticized [Wichter and Tollens (1911), Schorger (1917)]. Welbel and Zeisel (1895) advised weighing the precipitate in a weighing bottle because they believed it to be oxidized during drying and weighing in air. This contention was supported by Goodwin and Tollens (1904) and by Cunningham and Doree (1914), but denied by Mann, Krüger, and Tollens (1896), and Kröber (1900). Kröber (1901) found that on exposure to the air the precipitate took up moisture which was later removed with difficulty.

This conflicting evidence prompts the suspicion that the furfuralphloroglucinol precipitate does not have a fixed chemical composition. Various molecular proportions between furfural and phloroglucinol are cited by different writers, who further disagree as to the number of water molecules that are eliminated in the reaction. Goodwin and Tollens (1904) claimed that one molecule of water split out at ordinary temperature while at 80° C. three were lost. Kröber, in compiling his tables and formulas, assumed that two molecules were eliminated. Evidently, no two have had the same pure compound for analysis. The latest work is that of Votocek and Potmesil (1916) in which furfural was used to precipitate phloroglucinol from acid solution. These experimenters found, from a large number of determinations, that the ratio of condensation product to phloroglucinol was "about 2 : 1." Goodwin and Tollens and Kröber stated, however, that the variable composition of the precipitate could probably be disregarded without introducing any appreciable error. This is due to the purely empirical nature of the method.

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[1] Part I of this article was published in the previous issue of THIS JOURNAL.

[2] For references see bibliography at end of article.

Barbituric Acid Derivatives—The use of barbituric acid was suggested by Conrad and Reinbach (1901), and developed by Jäger and Unger (1902, 1903). Fromherz (1907), and Dox and Plaisance (1916) criticized the method, and the latter investigators also found malonylguanidine to be unsatisfactory. They found, however, that thiobarbituric acid precipitated furfural quantitatively from acid solution as a definite, crystalline chemical compound. They also suggested that the proportions of methylfurfural and furfural present could be calculated from the nitrogen and sulfur content of the precipitate. Hydroxymethylfurfural did not interfere.

Sodium Bisulfite—Jolles (1905) proposed the addition of an excess of standard sodium bisulfite solution to a neutralized aliquot of the distillate and titration of the excess by iodine. He also estimated both pentoses and methylpentoses by precipitating the former as barium pentosate [Bey (1900)] and performing a double distillation [Jolles (1907)]. The method was studied by Tolman and Trescott (1906) and Kerp and Wöhler (1909), who found that conditions had to be closely duplicated to obtain concordant results.

Fehling's Solution—The reduction of Fehling's solution by furfural was proposed as a possible method by Flohil (1911) and further studied by Eynon and Lane (1912) and by Baker and Hulton (1916), who found the presence of sodium chloride to be an influencing factor.

Silver Oxide—The oxidation of furfural by ammoniacal silver oxide was used in a volumetric procedure by Cormack (1900), who titrated the excess silver by thiocyanate after filtration of the silver precipitate. Cormack's method has never been applied to the determination of pentoses.

Present Official Method

The method of the Association of Official Agricultural Chemists (1920) is essentially the Kröber modification of the Tollens method. To the distillate obtained, as previously described, an amount of phloroglucinol double that of the furfural expected is then added and the volume made up to 400 cc. with 12 per cent hydrochloric acid and allowed to stand over night. The amorphous precipitate is filtered off, washed, dried, and weighed in a tared Gooch crucible. After applying a solubility correction, the corresponding weight of pentose or pentosan is calculated using Kröber's factors.

The principal points of criticism of the present method are:

1—The method is empirical and is not based on the molecular weight of the condensation product; moreover, solubility corrections are necessary [Dox and Plaisance (1916)].

2—Theoretical yields of furfural are rarely, if ever, obtained.

3—The actual yields of furfural are conditioned by the rate of distillation and by the concentration of acid [de Chalmot (1893, 1894), Councler (1894), Welbel and Zeisel (1895), Wenzel and Lazar (1913), Falada, Stein and Ravniker (1914), van Haarst and Olivier (1914), Kreeman and Klein (1917)]. The usual yields of furfural obtained are recorded in Table I.[3]

4—The various pentoses all yield different amounts of furfural. Kröber, therefore, as well as Tollens (1896), had to use a different factor in his calculations for each specific sugar. Hence an unknown material should be examined qualitatively. All the recorded data on the pentosans in wood are unreliable, since woods usually contain both araban and xylan [Schorger (1917), Schwalbe (1919)]. The presence of certain substances in the sample may prevent the liberation of the furfural [Seilliere (1909)].

5—Phloroglucinol precipitates substances other than furfural which are frequently present. Hydroxymethylfurfural, produced from hexose materials, is the chief one of these. [Düll (1895), Kiermayer (1895), Müther and Tollens (1904), van Ekenstein and Blanksma (1910), Jäger and Unger (1902), Kröber, Rimbach and Tollens (1902)]. The interference of this substance has been avoided by fermentation of the hexoses [Spoehr (1919)] and by redistilling the distillates [Fraps (1901), Cunningham and Doree (1914), Oshima and Konds (1918)]. The former method is inaccurate owing to fermentation of pentoses [Gillet (1917), Cross and Tollens (1912), Pellet (1916)], while in the latter method furfural is destroyed [Fraps (1901), van Haarst and Olivier (1914)]. Moreover, the fact that hydroxymethylfurfural phloroglucide is soluble in alcohol casts doubt on the existing methylpentosan data [Cunningham and Doree (1914)]. Schorger (1917) further points out that woods have never been proved to contain methylpentosans.

6—Substances other than pentose may yield furfural in the distillation. Glucuronic acid is the only compound for which this has been proved [Tollens (1909)], although oxycellulose, fats and oils, and their decomposition products are said to yield furfural [Bray and Staidl (1922)].

Experimental

Preliminary Tests

In the search for a satisfactory method for the determination of furfural, several procedures were tested out.

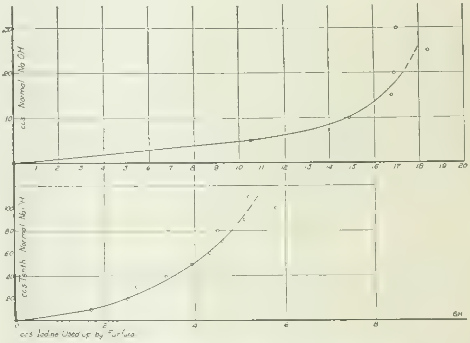

Fig. 1—Furfural Titrations with Hypoiodite

Sodium Hypoiodite—It was at first thought that iodine would be suitable. This reagent reacted with furfural only in alkaline solution. Moreover, the amount of iodine taken up was almost a direct function of the alkalinity, if the latter was low, as indicated in Fig. 1, while in strongly alkaline solutions concordant results could not be obtained. Although the amount of iodine used up appeared to approach a maximum, the results could not be accurately duplicated.

Acid Permanganate—Acid permanganate was then tried, but soon abandoned because large and indefinite volumes of permanganate were reduced to manganese dioxide by small quantities of furfural.

Potassium Bromate—At this point the use of potassium bromate was suggested by the work of Okuda (1919) on the oxidation of cystine. This reagent reacts as follows in acidified potassium bromide solution [Treadwell and Hall (1919)]:

$$KBrO_3 + 5KBr + 6HCl = 3Br_2 + 6KCl + 3H_2O$$

According to Wedekind (1901) furfural can be readily oxidized and brominated in aqueous solution. It was therefore hoped that the reaction between furfural and bromine[4] could be made the basis of a satisfactory method for the determination of furfural, provided an accurate means of finding the end point could be devised. Okuda used the yellow color due to free bromine as indicating the end point. In a preliminary test it was found that this could more accurately be found by the use of a simplified electrometric apparatus. With the use of the latter, a study of the optimum conditions for the titration of furfural by potassium bromate in acidified potassium bromide solution was undertaken.

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[3] See Part I in the preceding issue of This Journal.

[4] After the work of the writers was completed, attention was called to the work of Van Eck ["Versl. v. d. Verricht. v. h. Centr. lab. v. d. Volksgezondh.," **1918**; *C. A.*, **14**, 509 (1920)], who attempted to determine furfural by adding an excess of 0.1 *N* bromine in potassium bromide and determining the excess bromine over that reacting with the furfural. Details of his method are not available. The writers have been unable to secure satisfactory results by any method which involves adding an excess of bromine.

MATERIALS

Two specimens of furfural were used, one of which was obtained from a supply house, while the other had been prepared by graduate students working in the department of chemical engineering. Both samples distilled at 159° to 160° C., giving pale straw-colored distillates. Under reduced pressure these gave water-white distillates, which were used in making up the furfural solutions. All the solutions titrated had been freshly prepared from colorless furfural only a few hours previously. Old furfural solutions usually gave results which were somewhat in excess of the theory. A weighed quantity of the furfural was dissolved in distilled water and made up to a definite volume, from which aliquots were withdrawn for analysis.

"Chemically pure" potassium bromate was used, which, after drying, gave on analysis 99.99 per cent $KBrO_3$. The 0.1 *N* solution requires 2.7837 grams per liter. The bromate solution was standardized according to the method recommended by Merck (1914), in which 30 to 40 cc. are added to an acidified potassium iodide solution and the mixture is allowed to stand several minutes, after which it is diluted and the iodine titrated with standard thiosulfate in the usual manner.

A 20 per cent solution of potassium bromide free from bromate was used.

APPARATUS

The apparatus used consists of a galvanometer, a tapping key, and two platinum wires, one of which is sealed into the side of a small pipet and held at a fixed potential by immersion in an acidified solution of 20 per cent potassium bromide containing a trace of free bromine. The other platinum wire is immersed in the solution to be titrated in a beaker. The potential of this wire depends upon the composition of the solution being titrated. A small electric stirrer insures thorough mixing of the unknown solution.

Before beginning the titration, depression of the tapping key will cause the galvanometer to deflect several divisions to the right or left, depending upon the exact manner in which the connections are made, whereas after the titration is completed, the presence of an excess of bromine in the beaker will cause a throw of the needle in the opposite direction. Obviously, when depression of the key causes no deflection, the potential of both platinum wires is the same and the concentration of free bromine in the solution being titrated is practically equal to that in contact with the other platinum wire in the pipet. This is the end point.

TABLE VI—EFFECT OF ACIDITY ON THE TITRATION OF FURFURAL SOLUTIONS
(0.1002 gram of furfural used in each case)

HCl Per cent	0.1 *N* $KBrO_3$ Cc.	Furfural Found (Factor = 0.004803) Gram	Recovery Per cent
1.4	20.70	0.0994	99.2
1.4	20.75	0.0997	99.5
1.4	20.85	0.1001	100.0
1.5	20.70	0.0994	99.2
2.6	20.80	0.0999	99.7
2.6	20.88	0.1003	100.1
2.7	20.85	0.1001	100.0
2.8	20.83	0.1000	99.9
4.0	20.55	0.0987	98.5
4.1	21.00	0.1009	100.7
4.2	20.80	0.0999	99.7
4.3	20.95	0.1006	100.4
5.0	21.00	0.1009	100.7
5.2	22.60	0.1085	108.4
5.2	22.25	0.1069	106.7
5.3	22.15	0.1064	106.2
6.8	24.52	0.1178	117.6
7.0	25.00	0.1201	119.8
7.0	25.40	0.1220	121.8
7.2	24.80	0.1191	118.9

METHOD

In the preliminary experiments the titrations were carried out as follows: The bromate solution was added to the furfural solution rather slowly until near the end point, when three to five drops were added at a time until the point was found at which, at the end of 2 minutes, a mere trace of free bromine was present as indicated by no deflection of the needle on closing the galvanometer circuit. This was taken as the end point. Since the molecular ratio of furfural to potassium bromate was unknown, equal quantities of furfural were always used so that the buret readings would serve as an index to the accuracy of the work. The factor for converting the standard bromate solution into furfural was computed later (Table XI). It was used in this place to facilitate comparisons.

FACTORS AFFECTING THE TITRATION

ACIDITY OF THE SOLUTION—To 10-cc. volumes of a furfural solution 10 cc. of 20 per cent potassium bromide were added and the resulting solution diluted to about 100 cc. Varying amounts of hydrochloric acid were then added and the furfural was titrated with potassium bromate as already described. After titration of the furfural, 10 cc. of the solution were withdrawn and the acidity was determined by titration with standard alkali. The results are shown in Table VI. It is evident that the degree of oxidation of the furfural is a function of the acidity of the solution, but at low acidities (1.4 to 4.3 per cent hydrochloric acid) the process stops at the first stage and the further action of bromine takes place

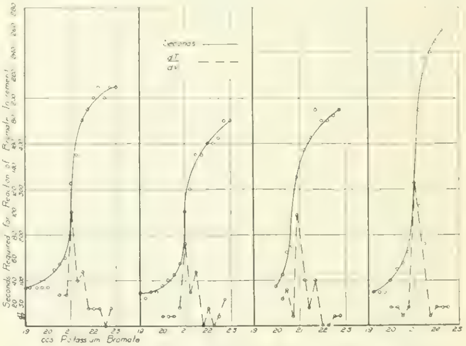

FIG. 2—TITRATION OF FURFURAL WITH BROMINE ($KBrO_3$ + HCl)

TABLE VII—EFFECT OF SPECIFIC ACID USED
(0.1006 gram furfural used in each case)

Per cent by Weight	0.1 *N* $KBrO_3$ Cc.	Furfural Found (Factor = 0.004803) Gram	Recovery Per cent
	Hydrochloric Acid		
3.8	21.00	0.1009	100.3
4.0	20.75	0.0997	99.1
4.1	21.00	0.1009	100.3
	AVERAGE	0.1005	99.9
	Sulfuric Acid		
5.0	20.85	0.1001	99.5
4.2	20.85	0.1001	99.5
4.5	20.90	0.1004	100.2
4.0	20.75	0.0997	99.1
3.5	20.90	0.1004	100.2
6.0	21.00	0.1009	100.3
4.1	21.00	0.1009	100.3
4.2	20.80	0.0999	99.2
	AVERAGE	0.1003	99.8

TABLE VIII—EFFECT OF CONCENTRATION OF POTASSIUM BROMIDE
(0.1002 gram furfural used in each case)

KBr Per cent	0.1 N KBrO$_3$ Cc.	Furfural Found Gram	Recovery Per cent
2.0	20.80	0 0990	99.7
1.0	20.75	0.0997	99.5
0.7	20.70	0.0994	99.2
0.5	20.90	0.1004	100.2
0.4	21.10	0.1013	101.2
0.4	21.40	0.1028	102.6
0.3	20.90	0.1004	100.2
0.3	22.00	0.1057	105.5
0.2	21.05	0.1011	100.9
0.2	21.35	0.1025	102.4
	AVERAGE	0.1012	101.1

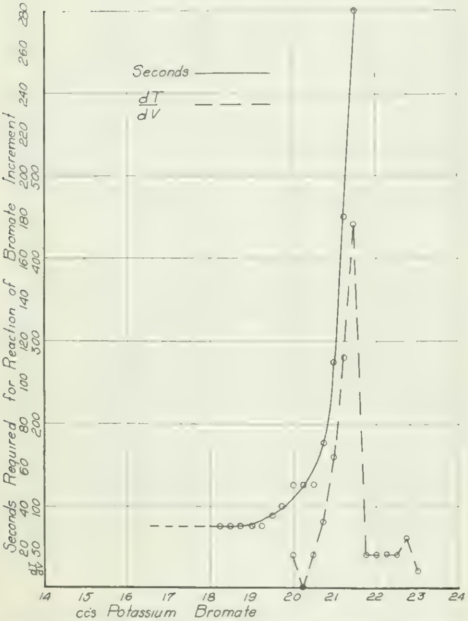

FIG. 3—ILLUSTRATION OF TYPICAL EXPERIMENT SHOWING HOW THE END POINT OF THE TITRATION IS OBTAINED

only slowly. A more accurate study of this last point is discussed later. In the most weakly acid solutions the reaction appeared to occur rather slowly, so that the bromate could only be added drop by drop. When the acidity was 3 to 4 per cent, however, the bromine was liberated promptly and therefore much less time was required for the titration. Moreover, accurate results were easily obtained provided the acidity did not exceed 4 per cent. This acidity was therefore adopted as standard.

SPECIFIC ACID USED—The substitution of 4 per cent sulfuric acid by weight for hydrochloric acid had no influence on the results, as is shown in Table VII.

CONCENTRATION OF POTASSIUM BROMIDE—The second factor studied was the influence of the concentration of potassium bromide on the results. Solutions containing 0.1002 gram of furfural, 10 cc. of 20 per cent potassium bromide, and 3 to 4 per cent hydrochloric acid in total volumes varying from 100 to 1000 cc. were titrated with bromate. The results appear in Table VIII. It is apparent that the concentration of potassium bromide does not consistently affect the titration. The irregular results are due to the fact that at the time these determinations were made the end point had not been carefully studied. A concentration of 1 per cent potassium bromide was used in all subsequent determinations.

TABLE IX—EFFECT OF CONCENTRATION OF FURFURAL
(0.1002 gram furfural used in each case)

Furfural Per cent	0.1 N KBrO$_3$ Cc.	Furfural Found (Factor 0.004803) Gram	Recovery Per cent
0.10	21.10	0.1013	101.2
0.06	20.60	0.0989	98.8
0.05	20.90	0.1004	100.2
0.03	21.10	0.1013	101.2
0.02	21.05	0.1011	100.9
0.01	21 10	0.1013	101.2
0.01	20.95	0.1006	100.4
0.005	21 15	0.1016	101.4
	AVERAGE	0.1008	100.7

TABLE X—EFFECT OF RATE OF ADDITION OF BROMATE SOLUTION
(0.1002 gram furfural used in each case)

0.1 N KBrO$_3$			
Added Rapidly at Start Cc.	Final Titer Cc.	Furfural Found (Factor = 0.004803) Gram	Recovery Per cent
18.00	21.20	0.1018	101.6
19.00	21.45	0.1030	102.8
20.50	21.75	0.1045	104.3
	AVERAGE	0.1031	102.9
Added Slowly from Start Cc.			
20.70		0.0994	99.2
20.75		0.0997	99.5
21.00		0.1009	100.6
	AVERAGE	0.1000	99.8

CONCENTRATION OF FURFURAL—In Table IX are brought together the results of trials in which the concentration of furfural was varied while that of both hydrochloric acid and potassium bromide was maintained constant. It was concluded from these results that, within the limits studied, the concentration does not affect the accuracy of the titration.

RATE OF ADDITION OF BROMATE—In Table X are recorded some results in which the bromate solution was added rapidly until the end point was nearly reached. After all the bromine had disappeared the titrations were finished in the usual way. However, the results ran too high, showing that it was necessary to add the reagent slowly, avoiding the presence of any large excess of free bromine if accurate results were to be expected. In all subsequent work, therefore, the bromate was added slowly enough so that the solutions were never more than faintly yellow colored.

THE END POINT—Having established the proper acidity and concentration of bromide required for the titration, the next problem was to improve the technic so that more concordant results might be obtained.

Towards the end of the reaction between furfural and bromine the oxidation is quite slow so that the oxidation potential of the solution is never constant. Therefore, the potentiometric method of determining the end point was not found suitable. It was then decided to determine the end point by using the time factor itself in connection with the titration apparatus already described.

For this purpose solutions of known furfural content were titrated to within 2 or 3 cc. of the end point, when the addition of the bromate solution was continued in 0.25-cc. increments. The time required for each increment to interact was observed by the use of the galvanometer and a watch. As soon as the deflection fell to zero the next increment of bromate was added and the process repeated until the end point had been crossed. The time required for disappearance of the bromine was then plotted against the total volume of potassium bromate that had been added. Several characteristic curves are shown in Fig. 2. The shape of these curves indicates that there are two possible reactions between furfural and bromine, but that one of these is far more rapid than the other in the presence of 4 per cent acid. This causes the curves to rise almost perpendicularly after the principal reaction has been completed.

The selection of the end point from such curves is rather difficult. If, however, the value dt/dv, where dv is the increment of bromate added and dt is the increase in time required for its disappearance over that required by the preceding increment, is plotted against the total volume of bromate used, a curve is obtained which passes through a maximum at the end point. This is best shown by the specific example given in Fig. 3. The lower set of curves in Fig. 2 shows the advantage of this method of plotting the results. Each upper and lower curve was plotted from the same data. Thus, the end point of the titration is obtained by measuring the time required for 0.25-cc. increments of bromate to react and plotting *dt/dv* against the total volume. The abscissa corresponding to the point of maximum inflection of the curve is the true end point.

The results of a series of determinations on known solutions of colorless furfural run according to the foregoing procedure are recorded in Table XI. Since this procedure appeared eminently satisfactory, the factor for converting bromate to furfural was calculated from the results.

TABLE XI—ANALYSES OF FURFURAL BY THE PROPOSED METHOD

Furfural Used Gram	0.1 *N* $KBrO_3$ Cc.	Factor Gram Pentose per Cc. 0.1 *N* $KBrO_3$	Furfural Found (Factor = 0.004803) Gram[a]	Recovery Per cent
0.1007	21.00[a]	0.00480	0.1009	100.1
0.1007	21.00[a]	0.00480	0.1009	100.1
0.1007	20.90[a]	0.00482	0.1004	99.7
0.1007	21.10[a]	0.00477	0.1013	100.6
0.1007	21.05	0.00478	0.1010	100.3
0.1007	20.85	0.00483	0.1001	99.4
0.1007	20.95	0.00481	0.1006	99.9
0.2014	42.00	0.00480	0.2017	100.1
0.2014	42.00	0.00480	0.2017	100.1
0.2014	41.95	0.00480	0.2014	100.0
0.2014	42.05	0.00479	0.2018	100.2
0.2014	42.05	0.00479	0.2018	100.2
0.1030	21.40	0.00481	0.1027	99.7
0.1030	21.50	0.00479	0.1032	100.2
0.1030	21.60	0.00477	0.1037	100.6
0.1030	21.50	0.00479	0.1032	100.2
0.1030	21.50	0.00479	0.1032	100.2
0.2060	43.25	0.00476	0.2076	100.8
0.2060	43.00	0.00479	0.2064	100.2
0.2060	43.25	0.00476	0.2076	100.8
0.2060	43.00	0.00479	0.2064	100.2
	AVERAGE	0.004792		100.2
	THEORETICAL	0.004803		100.0

[a] The curves for these results appear in Fig. 2.

A comparison of the results in Tables VI to X with those in Table XI shows much greater concordance in the latter. This suggests that the cause of error when an arbitrary 2-minute end point was used was probably the effect of small variations in acidity of the solution. However, such variations apparently affect both the reactions between furfural and bromine to nearly the same extent, so that when the results are plotted the end point is still readily located.

To verify this statement a final set of experiments was carried out in which the acidities were varied. The results are shown in Table XII and plotted in Fig. 4. The intensifying effect of the acid is clearly apparent from the slope of the upper set of curves. Nevertheless, the end points were readily found by replotting the data in the manner advised above.

TABLE XII—ANALYSES OF FURFURAL BY THE PROPOSED METHOD IN SOLUTIONS OF VARYING ACIDITIES
(0.1112 gram furfural used in each case)

HCl by Weight Per cent	0.1 *N* $KBrO_3$ Cc.	Furfural Found Gram	Recovery Per cent
1.8	23.15	0.1112	100.0
4.0	23.15	0.1112	100.0
5.0	23.00	0.1105	99.3
6.1	23.25	0.1117	100.4
	AVERAGE	0.1111	99.9

CONVERSION FACTOR FOR FURFURAL

The factors in Table XI were obtained by dividing the number of cubic centimeters of 0.1 *N* potassium bromate used by the corresponding weight of furfural. A close agreement is apparent, the average being 0.004792. Moreover, the theoretical ratio, based on a molecular ratio of potassium bromate to furfural of 1:3, is 0.004803, from which the experimental factor differs by less than 0.3 per cent. This is well within the limits of experimental error of the method so that the use of the theoretical factor for the purpose of calculation is justified. Theoretical factors were used throughout in the present studies, a procedure which is impossible in the present official method for determining furfural and pentoses.

EFFECT OF INTERFERING SUBSTANCES ON THE PROPOSED METHOD

Furfural distillates from pentose-containing materials always contain levulinic acid and hydroxymethyl-furfural when hexose materials are present. Therefore, a study of the possible effect of these substances was undertaken.

TABLE XIII—EFFECT OF LEVULINIC ACID
(0.2016 gram furfural used in each case. Total volume before titration 100 cc.)

Levulinic Acid Added Grams	0.1 *N* $KBrO_3$ Cc.	Furfural Found (Factor = 0.004803) Gram	Recovery Per cent
0.3	41.90	0.2012	99.8
1.0	42.05	0.2020	100.2
2.0	42.00	0.2017	100.1
3.0	41.80	0.2008	99.6
5.0	42.00	0.2017	100.1
	AVERAGE	0.2015	100.0
0	42.00	0.2017	100.1
0	41.80	0.2008	99.6
0	42.15	0.2024	100.4
0	42.00	0.2017	100.1
	AVERAGE	0.2016	100.0

LEVULINIC ACID—Five determinations were run on furfural solutions containing varying amounts of Kahlbaum's levulinic acid. The results are recorded in Table XIII. It is evident that the presence of this substance had no influence on the results in the cases tried.

TABLE XIV—EFFECT OF HEXOSE CARBOHYDRATES
(2.0-gram samples used in each case)

Material Used	0.1 *N* $KBrO_3$ Cc.	Furfural Found (Factor = 0.004803) Gram	Furfural Per cent	Pentose Factor = 0.007505 Per cent
Glucose	1.00	0.0048	0.24	0.38
	0.50	0.0024	0.12	0.18
Sucrose	1.00	0.0048	0.24	0.38
	0.75	0.0036	0.18	0.28
Lactose	1.00	0.0048	0.24	0.38
	1.00	0.0048	0.24	0.38
Starch	0.75	0.0036	0.18	0.28
	0.75	0.0036	0.18	0.28
		AVERAGE	0.20	0.32

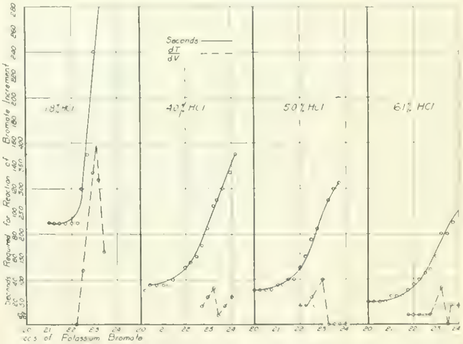

FIG. 4—TITRATION OF FURFURAL WITH BROMATE SOLUTION IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF HYDROCHLORIC ACID

HYDROXYMETHYLFURFURAL—Since no supply of this substance was available, weighed samples of glucose, sucrose, lactose, and starch were distilled by the method adopted for pentoses and the distillates titrated. The results are shown in Table XIV. As a further check, the determinations shown in Table XV were made, using mixtures of equal quantities of pentose and hexose. It is apparent from the results cited that hydroxymethyl furfural has a slight effect on the titration of furfural, but that this is small enough to be disregarded in many instances since the error thereby introduced is small.

TABLE XV EFFECT OF HEXOSES ON DETERMINATION OF PENTOSES
(0.3 gram each of xylose and sucrose used in each case)

0.1 *N* $KBrO_3$ Cc.	Pentose Found (Factor = 0.007505) Gram	Recovery Per cent
39.90	0.2994	99.8
40.10	0.3010	100.3
40.10	0.3010	100.3
40.25	0.3021	100.7
40.35	0.3028	100.9
40.40	0.3032	101.1
40.50	0.3040	101.3
40.50	0.3040	101.3
	AVERAGE	100.7

The probable explanation of the noninterference of hexoses seems to be that the hydroxymethyl furfural is converted, under the conditions of distillation, into levulinic acid, which is without effect.

0.1 *N* $KBrO_3$	Time Sec.	dT Sec.	dV Cc.	$\frac{dT}{dV}$
18.30	30	..	0.25	...
18.55	30	0	0.25	0
18.80	30	0	0.25	0
19.05	30	0	0.25	0
19.30	30	0	0.25	0
19.55	35	5	0.25	20
19.75	40	5	0.25	20
20.00	50	10	0.25	40
20.25	50	0	0.25	0
20.50	50	0	0.25	40
20.75	70	20	0.25	80
21.00	110	40	0.25	160
21.25	180	70	0.25	280
21.50	290	110	0.25	440
21.75	300	10	0.25	40
22.00	310	10	0.25	40
22.25	320	10	0.25	40
22.50	330	10	0.25	40
22.75	345	15	0.25	60
23.00	350	5	0.25	20

0.1 *N* $KBrO_3$ required 21.50 cc.
Furfural found 0.1033 gram
Recovery 100.3 per cent

METHYLFURFURAL—Inasmuch as methylfurfural might be expected to interfere, distillations of a methylpentose (rhamnose) were carried out. The rhamnose was prepared in this laboratory from quercitrin according to the method of Walton (1921) from the quercitrin in "lemon flavin." The rhamnose was analyzed and was found to be $C_6H_{12}O_5.H_2O$. The bromate titration values are shown in Table XVI. These indicate a recovery of 107 per cent using the same molecular ratio —i. e., $3C_6H_{12}O_5.H_2O:KBrO_3$—as was found for the pentose sugars. No explanation can be offered for this high value. There is no good evidence as to how widely methylpentosans are distributed in nature. These determinations indicate that if they are present they will form methylfurfural, which will be titrated in the proposed method and perhaps cause appreciable error in the pentosan values. Such an error, however, is present in all methods which have so far been proposed for pentosan derivatives, and it is believed that the bromate titration error will be much less than that incurred in the phloroglucinol method, owing to the other sources of error already present in that method.

From a study of these results the following method for the determination of furfural in aqueous solutions is suggested:

PROPOSED METHOD FOR DETERMINATION OF FURFURAL

To the solution containing 0.1 to 0.2 gram furfural, 5 cc. of 20 per cent potassium bromide are added for every 100 cc. of solution, and the acidity (HCl) is adjusted to about 4 per cent by weight by adding either acid or alkali as required. With continual stirring, 0.1 *N* potassium bromate solution is run in from a buret at such a rate that the production of a distinct yellow color throughout the solution is avoided. When the end point is approached a pale yellow color will be apparent immediately after the addition of a few drops of bromate solution, but this soon fades. When this point is reached the bromate is added in 0.2 to 0.3-cc. increments and the time is recorded which is required for the disappearance of free bromine, as indicated by the use of a galvanometer set-up as already explained. As the end point is crossed a rather large increase in the time required will be noted. The observations should be carried slightly beyond this point. Finally, the ratio of increment of time to increment of standard potassium bromate is plotted against the total value of potassium bromate already used, and the end point found from the curve thus obtained. The number of cubic centimeters of 0.1 *N* potassium bromate required multiplied by 0.004803 gives the grams of furfural in sample.

CONCLUSION

The studies concerning the potassium bromate method for the determination of furfural led to the following conclusions:

1—The acidity of the solution to be titrated should not exceed 4 or 5 per cent by weight, because

2—Further oxidation of the primary product of the interaction of bromine and furfural results in the presence of high concentrations of acid.

3—The velocity of this secondary reaction under the conditions proposed appears to be so small as to be without appreciable effect on the titration.

4—Either hydrochloric or sulfuric acids may be used.

5—An approximate concentration of 1 per cent potassium bromide is satisfactory.

6—The potassium bromate solution must be added slowly, at all times avoiding the presence of any considerable excess.

7—The amount of furfural present does not influence the accuracy of the method.

8—In titrating dilute solutions with potassium bromate, the end point can be readily located by the use of a simplified electrometric apparatus consisting of two platinum wires, a galvanometer, and key.

9—The time factor of the reaction involved is made the basis of the foregoing method for finding the end point.

10—Hydroxymethylfurfural, a product of the acid distillation of hexose materials, apparently interferes slightly with the use of the proposed method. However, the effect is small enough to be disregarded.

11—Levulinic acid, a further decomposition product of hexoses, is without any effect whatsoever.

12—Methylpentoses or pentosans will interfere in that methylfurfural is formed which will titrate with the bromate solution.

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The Influence of Neutral Salts upon the Fixation of Tannin by Hide Substance[1,2]

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Any agent which will decrease the swelling of collagen, or decrease its potential difference against the solution in contact with it, should inhibit the rate of fixation of tannin. Neutral salts should accomplish both effects, as predicted by the Donnan equilibrium,[3] shown by Procter and Wilson,[4] and recently definitely settled by Loeb.[5] On the acid side of the isoelectric point of the protein the anion only of the salt is concerned in this depressing effect, divalent anions being more effective than monovalent anions at identical hydrogen-ion concentrations. On the alkaline side of the isoelectric point cations only are of significance, again those of higher valency showing the greater depressing effect at the same concentrations of hydrogen ion. This "salt effect" on the protein is complicated, in the case of vegetable tanning, by additional action of the salt upon the tannin solution.

It has been shown by Wilson and Gallun[6] and by Thomas and Foster[7] that neutral salts decrease or retard the fixation of chrome by hide substance, while Herzog and Adler[8] claim that neutral salts either slightly promote the adsorption of phenol by hide substance or have no effect at all. In view of reported differences in behavior in the adsorption of these various tanning agents by collagen in the presence of neutral salts, it was decided to extend the study of tannin fixation by collagen to include the effect of added neutral salts in the tanning liquors.

Experimental

Sodium chloride and sodium sulfate, furnishing examples of monovalent and divalent anions, were selected for these experiments, and their effects at pH values of 2.0, 5.0, and 8.0 were studied in both hemlock bark and in gambier solutions. The tannin solutions were prepared and clarified as described in a previous paper.[9] It was also desired to include a study of tannin fixation in the presence of barium and magnesium chlorides in order to compare the effects of these divalent cations with that produced by the monovalent sodium cation. However, difficulties arose on the alkaline side of pH = 5 owing to the formation of the insoluble alkaline earth tannates, and consequently the study of the comparative effect of cations of different valence on the alkaline side of the isoelectric point of collagen was abandoned. The results obtained with these salts on the acid side of the isoelectric point were very similar to those obtained with sodium chloride, as was to be expected.

In the case of sodium chloride and sodium sulfate 100-cc. portions of the tanning solution (concentration of 40 grams total solids per liter, and previously adjusted to the desired pH by addition of 0.5 *M* hydrochloric acid or 0.5 *M* sodium hydroxide) were added to bottles containing 2.000-gram portions (absolutely dry basis) of hide powder, previously defatted by chloroform, and the required weight of dry salt. The bottles were rotated at room temperature for 24 hours; the samples were then filtered in Wilson and Kern extractors, washed with water until a negative test was shown by the washings for the salt used as well as for tannins and non-tans, dried, and the increase in weight was computed as tannin fixed. Since at certain concentration of hydrogen ion the salts precipitate "insolubles" which would count as tannin fixed, blanks were always run in the absence of hide powder to determine the extent of the formation of such "insolubles" and, where found, the amount of tannin fixed was corrected accordingly.

Results

The results are shown in the tabulation and figure.

Influence of Sodium Chloride and Sodium Sulfate upon Tannin Fixation[a]

pH of Original Liquor	Molar Concentration of Added Salt Present	Gambier[b]		Hemlock Bark[b]	
		NaCl	Na_2SO_4	NaCl	Na_2SO_4
2.0	0.5	47 loss	56 loss	58 loss	70 loss
2.0	1.0	62 loss	82 loss	66 loss	86 loss
2.0	1.5	....	90 loss	....	....
2.0	2.0	94 loss	....	68 loss	....
5.0	0.5	4 gain	17 loss	27 gain	8 loss
5.0	1.0	5 gain	50 loss	....	23 loss
5.0	1.5	....	75 loss	....	54 loss
5.0	2.0	4 loss	....	No change	....
8.0	0.5	32 loss	58 loss	9 loss	14 loss
8.0	1.0	63 loss	79 loss	25 loss	44 loss
8.0	1.5	...	92 loss	....	70 loss
8.0	2.0	86 loss	....	56 loss	....

[a] Compared with fixation in absence of salt.
[b] Figures are in per cent.

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[2] Contribution No. 419 from the Chemical Laboratories, Columbia University. Taken from a part of the dissertation submitted by Miss Kelly in partial fulfilment of the requirements for the degree of doctor of philosophy, Faculty of Pure Science, Columbia University, 1923.

[3] *Z. Elektrochem.*, **17**, 572 (1911).

[4] *J. Chem. Soc. (London)*, **109**, 307, 1327 (1916).

[5] "Proteins and the Theory of Colloidal Behavior," McGraw-Hill Co., New York, 1922. *J. Gen. Physiol.*, **1918-22** (about 50 papers published).

[6] *J. Am. Leather Chem. Assoc.*, **15**, 273 (1920).

[7] This Journal, **14**, 132 (1922).

[8] *Kolloid-Z.*, **2**, Suppl. Heft 2, III (1919).

[9] Thomas and Kelly, This Journal, **15**, 1148 (1923).

It is to be noted from the tabulation that at pH of 2 and 8 both salts inhibit the fixation of tannin, this effect increasing with increasing concentration of the salt, and for the same molar concentration of salt the inhibition by sodium sulfate is always more pronounced than that caused by sodium chloride, just as Thomas and Foster[10] found in the case of chrome tanning. At pH = 5, the isoelectric point of collagen, the effect of the added salts is much less pronounced, and for the lower concentrations sodium chloride appears to increase the fixation of tannins.

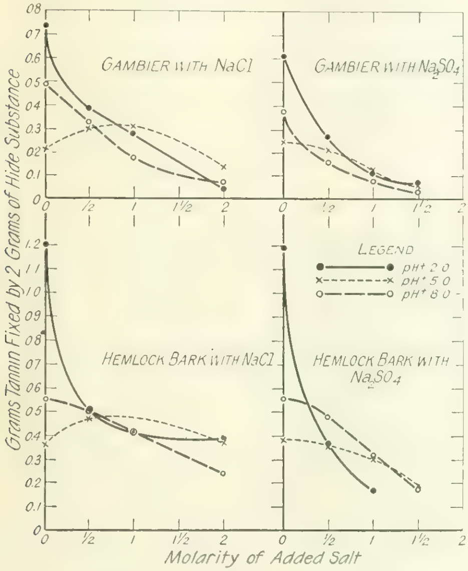

Fig. 1

Since Thomas and Baldwin[11] have found that sodium chloride increases the concentration of hydrogen ion (hydrogen-ion activity) of acid solutions, while sodium sulfate lowers it, measurements of the pH of the tanning liquors, after addition of the salts, were attempted in order to determine whether changes in hydrogen-ion concentration had been a determining factor in effecting the changes observed in tannin fixation. The results showed that at pH values of 2 and 5 sodium chloride was without appreciable effect upon the pH of the tanning solution, while sodium sulfate caused a slight decrease in acidity. At pH = 8 the measurements were most unsatisfactory, owing to "poisoning" of the electrode. Apparently, therefore, the effect of these salts in changing the hydrogen-ion concentration of the tanning liquors was not of any considerable importance, and the explanation for the observed changes in tannin fixation must be sought in the effects, pointed out above, of salts upon collagen and tanning solution.

Effect upon Collagen—It would be expected that on the acid side of the isoelectric point sulfates would have a greater depressing effect than chlorides upon swelling and potential difference of collagen, and consequently fixation should be inhibited more by the sulfate than by the chloride, which is actually the case as will be seen upon examination of the figures at pH = 2. At pH = 8 the differences between sodium chloride and sodium sulfate are not so marked. On this, the alkaline side of the isoelectric point, the anions of the salt exert the same influence regardless of valence. Here the cations only are of significance and the greater inhibitory effect shown by sodium sulfate is due to the fact that equimolar solutions of the two salts are being compared. Since there are twice as many available sodium ions in a molar solution of the sulfate as in the chloride, compared on the molar basis, sodium sulfate will lower the swelling and the potential difference of collagen to a greater extent than sodium chloride, as the data show. In the table it is seen that 0.5 *M* sodium sulfate shows about the same inhibition as 1.0 *M* sodium chloride. Such agreement is not expected to be rigid and general throughout, since the effects of the salts upon the tannins must be considered. Furthermore, ionization of the salts is by no means complete at such concentrations, nor are the salts ionized to the same extent. At the isoelectric point the effects of the salts upon collagen should not be marked, according to the Donnan theory, since at this point collagen is already in the condition of minimum swelling and minimum potential difference.

Influence on the Tanning Solutions—(1) Aggregation of the tannin particles, which will result in a lower diffusibility thereof, thus inhibiting fixation, but which may proceed to the point at which the tannins are precipitated ("salted out") from solution, whereby the concentration of tannin in solution is decreased; (2) hydration of the added salts, by which a virtual increase in tannin concentration is effected. The net effect of these two factors upon tannin fixation will depend upon the original concentration of tanning solution as well as upon the amount by which this concentration is increased or decreased. At a concentration of 40 grams of total solids per liter, which was used in these experiments, reference to the concentration curves in a separate paper[9] for the extracts in question shows that any increase in concentration of the extract at pH = 5 will effect a decrease of fixation of tannin, while decrease in concentration from 40 to approximately 20 grams of total solids per liter will cause an increase in tannin fixed, below which concentration the amount of tannin fixed will decrease regularly toward zero.

As will be seen by reference to the tables, this decrease in concentration of tannin by sodium chloride at pH = 5 is slight enough at the lower concentrations of the salt to effect the increase in fixation which would be expected, while for the higher concentrations of the salt the salting out effect has lowered the concentration of tannin sufficiently to effect a decrease in tannin fixation. Hydration of the salt and lowered diffusibility resulting from aggregation of the tannin particles will augment this latter factor.

On the other hand, the experimental results at pH = 5 show that sodium sulfate produces a decrease in fixation at all concentrations, thus differing from sodium chloride. Experiments upon the comparative effects of these two salts in salting out the tannins from tan liquors showed that the sulfate is more effective than the chloride. Consequently, it may be concluded that sodium sulfate decreases the degree of dispersion of tannin particles and effects subsequent reduction of concentration of tannins in solution more powerfully than sodium chloride, and only the later effect of this decreased concentration, augmented by increased aggregation of the particles and by the hydration factor, is shown in the experimental results obtained.

Acknowledgment

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[10] This Journal, **14**, 132 (1922).

[11] *J. Am. Chem. Soc.*, **41**, 1981 (1919)

Chemistry of Wood[1]

VII—Relation between Methoxyl and Lignin in Wood

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The isolated lignins from the two classes of woods differ in chemical composition. A larger per cent of the total methoxyl is recovered in softwood lignin than in hardwood lignin.

Approximately 62 per cent of the total methoxyl in white oak and yellow pine sawdust was recovered as methanol by treating the wood with dilute alkali under pressure. The methanol obtained by the dilute alkali and pressure treatment is equivalent in amount to the methoxyl found in the crude volatile products of the destructive distillation of wood.

It is indicated that the actual period of chlorination can be reduced approximately one-half in isolating cellulose.

IT IS a well-known fact that softwoods yield less methanol than hardwoods when subjected to destructive distillation. The difference in yields of methanol is even greater than would be expected when compared with the difference in the methoxyl content of the two classes of woods. Softwoods, in general, contain about 85 per cent as much methoxyl as hardwoods, although some softwoods contain more than some hardwoods. In destructive distillation the methanol yield from softwoods is approximately one-half that obtained from hardwoods.

This difference in behavior suggests that there is a difference in the linkage of the methoxyl group in the two classes of woods. A difference in the linkage of the methoxyl group is further suggested when the ratio of the methoxyl to the lignin content in the different woods is compared. For instance, tan oak[2] has a methoxyl content[3] of 5.74 per cent and a lignin content of 24.85 per cent. Yellow cedar has a methoxyl content of 5.25 per cent and a lignin content of 31.32 per cent. The ratio of the methoxyl to the lignin in the former wood is 23.1 per cent; in the latter wood it is 16.7 per cent. If, as is generally believed, the methoxyl is wholly associated with the lignin, then the chemical composition of the two lignins differs. If the methoxyl is only partially associated with the lignin, the two cases cited above indicate a different methoxyl linkage.

In order to obtain more detailed information on the manner in which the methoxyl is combined in the wood and on the relation between the methoxyl and the lignin, the following experimental studies were carried out: (1) methoxyl and the lignin content of various species; (2) methoxyl content of the isolated lignin of several species; (3) methoxyl liberated as methanol when different species are repeatedly treated with dilute alkali under pressure; (4) methoxyl and lignin content of the residues when different species are chlorinated for varying periods of time.

TABLE I—RELATION OF METHOXYL AND LIGNIN IN WOODS

SPECIES	Per cent Lignin in Wood (1)	Per cent CH_3O in Wood (2)	Per cent $\frac{CH_3O \times 100}{\text{Per cent Lignin}}$ (3)	Per cent CH_3O in Isolated Lignin (4)	Per cent CH_3O not Recovered in Isolated Lignin (Column 3 − Column 4) (5)
Western yellow pine	26.75	4.45	16.64	13.13	3.51
Western white pine	24.30	4.47	18.40	15.10	3.30
Incense cedar	37.68	6.09	16.16	14.51	1.65
Mesquite	30.77	5.49	17.84	14.05	3.79
Tan oak	24.68	5.70	22.06	16.99	5.07
Eucalyptus	26.74	6.56	24.53	15.01	9.52
Yellow poplar (sapwood)	23.86	5.89	24.69	17.00	7.69
Yellow poplar (heartwood)	23.69	6.03	25.45	20.22	5.23
Pignut hickory (heartwood)	22.85	5.79	25.34	18.43	6.91

EXPERIMENTAL WORK

METHOXYL AND LIGNIN CONTENT OF DIFFERENT WOODS—These determinations were made in the same manner as given in the preceding paper of this series on the chemistry of wood.[4] The results are given in Columns 1 and 2, Table I.

METHOXYL CONTENT OF ISOLATED LIGNIN—The methoxy content of the lignin, isolated by the method described in the preceding papers of this series, was determined by the Zeisel method. The results are recorded in Column 4, Table I. A comparison of Columns 3 and 4 shows that the theoretical and isolated lignins of softwoods are more nearly identical in chemical composition than the corresponding lignins of hardwoods. By subtracting the figures in Column 4 from the corresponding numbers in Column 3, the methoxyl not recovered in the lignin is obtained. A comparison of the corresponding values in Columns 3 and 5 indicates that from 10 to 21 per cent of the methoxyl in softwoods and from 21 to 38 per cent of the methoxyl in hardwoods are not recovered in the isolated lignin.

In order to show a different relationship between some of the constants given in Table I, the significant Columns 2 4, and 5 are all calculated on the dry weight of the wood and arranged in Table II. In Column 3, Table II, is found the methoxyl which is not recovered in the isolated lignins. Here again it is shown that the methoxyl not recovered in the isolated lignin is considerably less in the softwoods than in the hardwoods. This experimental fact, however, does not justify the conclusion that the methoxyl not recovered in the isolated lignin is associated with some chemical constituent other than lignin, for it may be removed as a cleavage product in the process of isolating the lignin. These results on hardwoods and hardwood lignins confirm those of Dore,[5] which are discussed by Ritter and Fleck.[6] In the case of softwood (redwood),[7] however, Dore was able to recover the total methoxyl of the wood in the isolated lignin. In the isolation of the redwood lignin the material was not boiled after diluting the sulfuric acid with hot water, whereas the lignin analyzed in this paper was boiled after diluting with water to aid coagulation of the material. In this latter case some methoxyl may have been hydrolyzed from lignin, and thus account for the results obtained.

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[1] Presented before the Division of Cellulose Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

[2] Same species as tanbark oak in Paper V of this series.

[3] THIS JOURNAL, **14**, 1150 (1922).

[4] THIS JOURNAL, **15**, 1055 (1923).

[5] *Ibid.*, **12**, 986 (1920).

[6] *Ibid.*, **14**, 1050 (1922).

[7] *Ibid.*, **12**, 475 (1920).

It is of interest to note that with the exception of eucalyptus the values in Column 3, Table II, agree closely with the yields of methanol obtained by destructively distilling the woods belonging to the corresponding classes.

Table II—Relation of Total Methoxyl to Methoxyl in Isolated Lignin

(Figures in percentages based on weight of original wood)

Species	CH_3O in Wood	CH_3O in Isolated Lignin	CH_3O not Recovered in Isolated Lignin
Western yellow pine	4.45	3.51	0.94
Western white pine	4.47	3.66	0.81
Incense cedar	6.09	5.46	0.63
Mesquite	5.49	4.30	1.19
Tan oak	5.70	4.19	1.51
Eucalyptus	6.56	4.01	2.55
Yellow poplar (sapwood)	5.89	4.05	1.84
Yellow poplar (heartwood)	6.03	4.79	1.22
Pignut hickory (heartwood)	5.79	4.21	1.58

Methoxyl Liberated as Methanol When Sawdust Is Treated with Dilute Alkali under Pressure—A 500-gram sample of sawdust which passed through a 40-mesh sieve was treated with 1500 cc. of 7 per cent sodium hydroxide solution. The mixture was placed in a large autoclave, which was heated in a nitrate bath. The temperature was raised gradually until an increase in pressure ranging from 115 to 120 pounds was noted. This pressure was maintained for 3 hours, after which it was released gradually and the distillate condensed. The distillate was treated in the regular standard method used at the Forest Products Laboratory for determining methanol in pyroligneous acid.[8] The residue in the autoclave was again thoroughly mixed with 600 cc. of water and the heating repeated at a still higher pressure. The residue was thus retreated, as shown by the table, until no methanol appeared in the distillate. The final residue was washed with hot water until neutral, dried, weighed, and analyzed for methoxyl.

White oak and western yellow pine sawdusts were treated as outlined above. The results are recorded in Tables III and IV.

The data show that repeated treatments of the sawdust with dilute alkali under increasing pressures gradually liberate 3.87 per cent methanol from white oak and 2.93 per cent methanol from western yellow pine. In the experiment the two woods yield the same percentages of total methoxyl—namely, 63 per cent—but the composition of the residues differs; the hardwood residue by analysis (Zeisel) contains the remaining methoxyl, whereas the softwood residue contains none. This again suggests a different methoxyl linkage in the two classes.

It is of interest to compare the yields of methanol obtained in this study with the percentage of methoxyl liberated as methanol in the crude volatile products by destructive distillation. In a paper by Hawley and Aiyar[9] are found the data given in Table V. The ratio of the methoxyl obtained in the volatile products to the total methoxyl in the three cases cited is approximately 62 per cent, the same as obtained in the volatile products by the alkali hydrolytic treatment of two woods. This suggests that the methanol recovered in this study comes from the same methoxyl groups found in the crude volatile products in destructive distillation.

Lignin and Methoxyl Content of Sawdust Residues after Varying Periods of Chlorination—In this study duplicate sawdust samples of known lignin and methoxyl content were extracted with a minimum boiling alcohol-benzene solution. The residues were then chlorinated for varying periods of time, and the lignin chloride formed was extracted with sodium sulfite. These residues were thoroughly washed with hot water, dried, and weighed.

These final residues were then analyzed for lignin and methoxyl to determine the relation between the ratios of lignin removed to total lignin and methoxyl removed to total methoxyl.

In Table VI, Columns 4 and 5, respectively, are found the percentages of total lignin and methoxyl in the residues after the various chlorinations. In the case of basswood the corresponding ratios in the two columns agree fairly well. With incense cedar the first corresponding ratios are at variance, the remaining three agree very favorably. The same data for tan oak show no agreement in the 10-minute chlorinated residue. The agreement is better in 15 and 20-minute chlorinated residues.

If the proportions of the total methoxyl and lignin were the same in the individual residues obtained by varying periods of chlorination, then the conclusion that *all the methoxyl is associated with the lignin and that all is combined*

Table III—Percentage of Methoxyl Recovered as Methanol from Sawdust Treated with NaOH Solution under Pressure

(Methoxyl content of original wood = 6.12 per cent = 6.31 per cent methanol. Moisture content of original wood = 7.00 per cent)

Species	Treatment	Dry Weight of Sample G.	Pressure for 3 Hours Lbs.	7 Per cent NaOH Added Cc.	Water Added Cc.	Methanol Obtained G.	Per cent Methanol on Dry Weight of Wood	Per cent Methoxyl Content
White oak	1	465	105 to 115	1500		9.86	2.12	
Residue from above	2		115 to 120		600	1.54	0.33	
	3		160 to 180		600	2.52	0.54	
	4		160 to 180		600	2.24	0.48	
	5		180 to 200		600	1.87	0.40	
	6		180 to 200		600	0.00	0.00	
Total alcohol in distillate						18.03	3.87	
Final residue		280						3.65
Methoxyl retained in residue calculated as methanol						10.55	2.26	
Total methoxyl accounted for as methanol in distillate and residue							6.13	

Table IV—Percentage of Methoxyl Recovered as Methanol from Western Yellow Pine Sawdust Treated with NaOH Solution under Pressure

(Methoxyl content of original wood = 4.55 per cent = 4.70 per cent methanol. Moisture content of original wood = 7.50 per cent)

Species	Treatment	Dry Weight of Sample G.	Pressure for 3 Hours Lbs.	7 Per cent NaOH Added Cc.	Water Added Cc.	Methanol Obtained G.	Per cent Methanol on Dry Weight of Wood
Western yellow pine	1	416	110 to 120	1500		6.11	1.47
Residue from above	2		140 to 160		600	2.49	0.60
	3		160 to 180		600	2.51	0.60
	4		180 to 200		600	1.08	0.26
	5		180 to 200		600	0.00	0.00
Total alcohol in distillate						12.19	2.93
Final residue		221	(Zeisel) no methoxyl				
Total methoxyl accounted for as methanol in distillate and residue							2.93

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[8] *U. S. Dept. Agr., Bull.* **29**, 5.

[9] This Journal, **14**, 1056 (1922).

in the same manner would be justified. This conclusion is substantiated in the case of basswood and incense cedar, but not in the case of tan oak.

In Table VI it will be noted that the chlorination periods were shortened in going from basswood to incense cedar. In basswood the 30 and 45-minute samples were not extracted with sodium sulfite after the first 15-minute chlorination, although they were stirred at 5-minute intervals. Columns 1 and 2, Table V, show very little lignin and methoxyl removed by the second 15-minute chlorination. The tan oak and incense cedar show how more frequent alternation of chlorination and sodium sulfite extraction may reduce the actual chlorination period in isolating cellulose. This has been studied more fully and will appear in a separate paper.

TABLE V—DISTRIBUTION OF METHOXYL IN PRODUCTS OF WOOD DISTILLATION

(Figures in percentages of dry weight of wood distilled)

PRODUCTS	Hard Maple 6.09 Per cent—CH_3O Blank	White Oak 5.12 Per cent—CH_3O Blank	Incense Cedar 5.9 Per cent—CH_3O Blank
Pyroligneous acid	1.62	1.16	0.97
Dissolved tar	0.34	0.22	0.10
Settled tar	0.52	0.46	1.04
Gas (calculated as CH_4)	1.31	1.34	1.60
Total methoxyl recovered in volatile products	3.79	3.18	3.71
$\frac{\text{Volatile}-CH_3O}{\text{Total}-CH_3O}$	62	62	63

TABLE VI—RELATION OF METHOXYL TO LIGNIN

(Figures are percentages calculated on dry weight of wood)

	Lignin	CH_3O	$\frac{CH_3O \times 100}{\text{Lignin}}$	$\frac{\text{Residual Lignin} \times 100}{\text{Total Lignin}}$	$\frac{\text{Residual } CH_3O \times 100}{\text{Total } CH_3O}$
Basswood					
Original wood	20.7	5.02	24.2	...	...
15-minute chlorination	5.16	1.23	23.8	24.9	24.5
30-minute chlorination[a]	5.06	1.01	20.0	24.4	20.1
45-minute chlorination	3.39	0.78	23.0	16.3	15.5
Tan oak					
Original wood	23.7	5.31	22.4	...	...
10-minute chlorination	5.29	2.34	44.2	22.3	44.0
15-minute chlorination	1.78	0.33	18.5	7.5	6.2
20-minute chlorination	1.38	0.17	12.3	5.8	3.2
Incense cedar					
Original wood	37.73	6.14	16.3	...	...
5-minute chlorination	10.7	1.10	10.3	28.3	17.9
10-minute chlorination	2.8	0.43	15.4	7.4	7.0
15-minute chlorination	1.0	0.16	16.0	2.6	2.6
20-minute chlorination	0.75	0.096	12.8	1.9	1.6

[a] Not extracted with sodium sulfite.

Charles Proteus Steinmetz

WHEN Charles Proteus Steinmetz died on October 26, 1923, science lost one of its unique figures. Born at Breslau, Germany, April 9, 1865, Dr. Steinmetz studied mathematics, physics, and kindred subjects at the University of Breslau, and it is curious to note that so great a mathematician in his younger years experienced much difficulty in learning the multiplication table. While at the university he espoused the cause of socialism, fell under the ban of the German Government, and was forced to leave the university and to flee the country. He continued his studies in Switzerland and was persuaded by an American student at the Polytechnic at Zurich to accompany him to America. He narrowly escaped rejection at the hands of the immigration officials, but within two weeks after admission was devoting his talents to the improvement of the electric street cars at Yonkers. In 1893 he joined the staff of the General Electric Company, and there found the congenial environment and support necessary for a genius like his to accomplish most for the benefit of mankind. Freed from financial worries, with the resources of a great corporation in coöperation with him, and provided with facilities for the furtherance of research, he was able to overcome one after another many of the obstacles in the way of electrical progress. His investigation in the field of magnetism, which led to formulating and determining the laws governing the losses in iron subjected to varying magnetic induction, was one of his first great pieces of work. It made possible the improvement of electrical machinery with the reduction in the weight and the cost. He abolished the mystery and obscurity surrounding alternating current apparatus and did much to teach engineers how to design machines with as much ease and certainty as those employing the familiar direct current.

Of late years, when alternating current power transmission lines carrying large amounts of energy spread over the country, he turned his talents to the study of the problem of protecting such lines from lightning. His study of the phenomena produced by lightning effects led him to produce his famous lightning generator which has been so much discussed in the public press.

Dr. Steinmetz's practical inventions literally cover the entire field of electrical applications, and of the two hundred or more patents in his name perhaps most important are the induction regulator, the method of phase transformation as from two phases to three phases, and the metallic electrode arc lamp. He was a prolific inventor, a skilled mathematician, a trained engineer, and an inspiring teacher, not only possessing marvelous insight into scientific phenomena, but a wonderful ability to explain in simple language the most difficult and abstruse problems. He was the author of many original scientific papers and books, was an ardent believer in the value of education, and was always willing to share his great gifts with any who sought his counsel. He was a patient, sympathetic, and cheerful man, with a fine appreciation of nature, and one who constantly made friends with children. He was an earnest, simple man, who devoted his mind and talents to the service of his fellow-men to an extraordinary degree.

His life was a successful one for he accomplished that for which he worked, and lived as pleased him.

LS Rubber—A New Crude Rubber[1]

By Ernest Hopkinson

UNITED STATES RUBBER CO., NEW YORK, N. Y.

This paper gives a general description of the methods of making the standard crudes—fine Para, pale crepe, and smoked sheet.

The apparatus for making sprayed rubber and the method of operation is described.

The merits of sprayed rubber as brought out during a period of three years' testing are given and tables are shown which give analytical data and physical tests of sprayed rubber in comparison with fine para, pale crepe, and smoked sheet.

Sprayed rubber is uniform in quality, ages well in cured stocks, gives high tensile strength, cures quickly, and is of broad application in the manufacturing of rubber goods.

THE methods of obtaining from latex the standard crude rubbers which appear on the market today are generally well known and need to be only briefly described here. Curiously enough, fine Para, which has generally been considered one of the best crude rubbers, is obtained by a very elemental method. The natives accomplish this by turning a stick or paddle which has been dipped in latex over a smoky fire until coagulation and evaporation take place, producing a film of rubber on the stick on which successive layers are added until the mass is of such size as to become unwieldy, when it is removed from the stick and sent to the market. Some of the nonrubber constituents of the latex are lost.

In the manufacture of crepe rubber on the plantations in the East, the latex as collected is brought to approximately a standard dilution of 20 per cent dry rubber content. If it is desired to make pale crepe, a solution of sodium bisulfite is added in the proportion of 1 part of bisulfite to 100 of latex. Acetic acid is employed as the coagulant and is usually added as a 5 per cent solution in such quantities as to give 0.1 per cent on the latex. Thorough agitation of the latex during coagulation is essential. The coagulum is washed to remove the acid by passing a few times through corrugated rolls and finally through smooth rolls. The number of passes through the creping rolls varies from five to ten, depending on whether or not the rubber is to be vacuum-dried or air-dried and also upon the thickness desired.

In making smoked sheet rubber, the latex, preferably bulked in lots of 50 gallons or more, is diluted to approximately a standard concentration of 15 per cent dry rubber content. No sodium bisulfite is added. Coagulation is effected by adding about 0.5 per cent on the latex of acetic acid as a 1 per cent solution. The coagulation is carried out in rectangular pans and the slabs of coagulum are passed a few times through smooth rolls and once through marking rolls. Smoking is continued until the sheets are dry, the process usually requiring from 9 to 10 days at a temperature of 110° to 120° F.

Blanket rubber is made in the same general way as crepe, and is milled thick prior to drying or it may be plied up from thin, dry crepe.

TABLE I—ANALYTICAL DATA OF CRUDES, PER CENT

	Ash	Acetone Extract	Water Extract	Sugars	Proteins
Fine Para	0.50	3.30	0.50	0.81	3.62
Pale crepe	0.30	3.20	0.40	0.30	2.94
Smoked sheet	0.31	3.10	0.85	0.30	2.40
LS rubber	1.10	4.25	6.50	1.40	4.20

Slab rubber is made by either natural or acetic acid coagulation and is not strictly a market grade. The slabs of coagulum are simply pressed or sheeted from 0.5 to 1 inch in thickness, and may be entirely dried or only surface-dried. Much trouble results from sliming because of the putrefaction, and an offensive odor is developed which may persist in cured goods. This rubber ordinarily cures in about half the time required for pale crepe in the 10 per cent sulfur compound. The quick-curing characteristics are due in part to the maturation or decomposition of the proteins, but the exact identity of the natural accelerator has not been determined.

LS RUBBER—SPRAYED RUBBER

In studying the methods by which crudes in common use have been prepared, the writer was impressed with the importance of giving very careful consideration to the solid constituents of latex not utilized by the usual methods of preparation. The study of the possibility of utilizing materials which, if of value, should very appreciably increase the world's rubber supply led to an investigation in the company's plantations in Sumatra and in its general laboratories at New York. The results of these investigations very soon established the fact that when prepared by certain methods rubber containing constituents not usually obtained by the coagulation methods, possesses qualities superior to the usual rubbers.

The apparatus for producing LS rubber which has so far given the best results and which is now being used commercially is known as the disk spray. In this process the latex is allowed to flow onto a rapidly revolving, horizontally mounted disk, from which it is thrown in an umbrella-shaped spray or mist into a heated current of air or inert gas. The disk is located at the top of a tower, generally of the shape of a hollow pyramid, and the fine spray of rubber globules falling through the hot air or gas settles on the bottom of the unit as a dry, creamy white, spongy mass, which has approximately one-third the apparent density of ordinary crepe rubber. A current of heated air is forced in at the top of the tower and escapes at the outer edge of the bottom of the unit, carrying the moisture with it. The rubber globules are dried almost instantly and the rubber shows no harmful effect whatever from heat required for evaporation. The heat is supplied from an oil-burning furnace and the temperature at the entrance and exit of the spray unit is easily and carefully controlled. The capacity of the spray unit is from 600 to 800 pounds of dry evaporated rubber per hour, varying with the total solid content of the latex used. This process of making rubber is continuous since the bottom of the unit consists of a movable platform by means of which the dry, spongy rubber is easily removed from the floor to the baler. The rubber, which is creamy white when deposited, takes on the appearance of commercial light brown crepe when creped or compressed.

CHARACTERISTICS OF LS RUBBER

CHEMICAL—In general, LS rubber has higher ash, water extract, acetone extract, and nitrogen content than either Para or plantation rubbers. (Table I) A portion of the water-soluble matter is also extractable by acetone, and corrections must therefore be made in determining these amounts. The water-soluble material consists of nitrogenous matter, sugars, and inorganic salts. The nitrogenous matter is largely colloidal. The sugars, which are of the inositol series, make up about 1 per cent of the rubber. The sugars dried during evaporation in the spray process are responsible for giving LS rubber its characteristic sweet odor. The inorganic salts are chiefly potassium phosphate, with traces of magnesium and calcium salts. This water-extractive material is hygroscopic, and because of its presence LS rubber contains normally about 1 per cent of moisture.

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[1] Presented before the Division of Rubber Chemistry at the 65th Meeting of the American Chemical Society, New Haven, Conn., April 2 to 7, 1923.

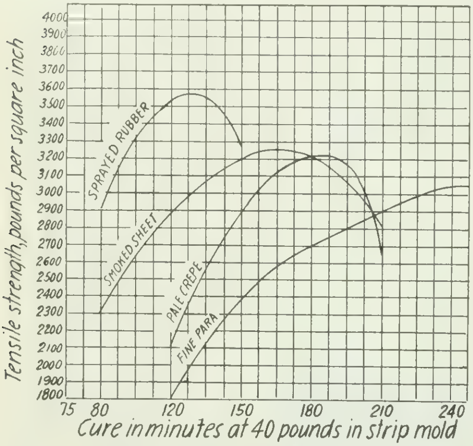


FIG. 1—AVERAGE TENSILE STRENGTH CURVE FOR TWENTY DIFFERENT LOTS OF EACH CRUDE IN 10 PER CENT SULFUR STOCK

PHYSICAL—A noticeable characteristic of LS rubber is its tough, nervy quality. This is attributed to two causes—the presence and nature of the nonrubber constituents, and the fact that the finished rubber is produced almost instantaneously from clean latex and therefore need not be subjected to washing, creping, smoking, drying, and various manipulations required for Para and plantation crudes. The color varies from light brown to dark brown, depending upon the amount of compression to which it is subjected in the baling process. The extra nervy quality of LS rubber is illustrated by comparing it with pale crepe on a standard mill under identical conditions, and the results of this test showed an increase for the LS rubber of approximately 15 per cent both in time required to break down and power consumption. The higher power consumption of LS rubber during milling was confirmed when the factories carried out works tests with this rubber. It is of interest, however, to note that when the factories worked with quantities of LS rubber made from regular production runs on the plantation in Sumatra, the difference in power consumption between this rubber and the standard plantation rubbers was smaller than that obtained in earlier experiments from rubber made in the experimental unit, and the harder milling qualities of the rubber have ceased to be of concern with the factories using it. The ability of LS rubber to absorb mineral fillers has not been found to be appreciably different from that of standard plantation rubbers. However, the LS rubber takes up oil during mixing appreciably faster than do the other rubbers.

In cured stocks LS rubber gives a higher tensile strength than any other crude, a slightly lower stretch, and a higher breaking set. In many cases a tensile strength in excess of 4000 pounds per square inch is obtained in the 10 per cent sulfur compound. Results obtained from such typical compound of LS rubber, Para, pale crepe and smoked sheet are given in Table II. In Fig. 1 is shown the average tensile strength curves of LS rubber, smoked sheet, pale crepe, and fine Para compiled from tests of twenty samples of each rubber. It may be noted that the LS rubber gives a tensile strength about 10 per cent greater than any of the others. The effective curing range of this rubber as a crude with 10 per cent sulfur covers a period of about 1 hour (good cures being obtained from 90 to 150 minutes at 40 pounds in a strip mold). In Figs. 2, 3, and 4, the curves of the tensile strength obtained for a number of tests made on LS rubber, smoked sheet, and pale crepe, respectively, are shown. Each curve for smoked sheet and pale crepe represents duplicate control tests on a regular shipment of these rubbers. Each LS rubber curve represents a test on a different lot of LS rubber made in the experimental unit. When it is considered that these lots of LS rubber were made from latex in which the percentage of preservative was not constant, which was shipped in different kinds of containers and which had been handled in different ways, the uniformity of the tests is considered to be remarkable. Moreover, from the fact that in no case have poor lots of LS rubber been obtained such as have been obtained in smoked sheet, pale crepe, and fine Para shipments, it is thought that it can safely be concluded that LS rubber is of more uniform quality than any other crude rubber which has been produced on a commercial scale. This is of great importance to the users of rubber, since it is a long-sought quality in crude rubber which has not been previously obtained by the producers of plantation rubber.

The abrasion qualities of stocks containing LS rubber are equal and in many cases superior to the same type of stocks made with standard rubbers. Inner tubes seem to have greater resistance to tearing if made with LS rubber.

RATE OF CURE—Another remarkable quality is the rapid-curing characteristic of LS rubber. For example, the cure for a few of the standard crudes with 10 per cent sulfur in a strip mold at 40 pounds steam pressure is for fine Para $^1/_2$ to 4 hours, for pale crepe 3 to $3^1/_2$ hours, smoked sheet $2^3/_4$ to $3^1/_2$ hours, and for LS rubber $1^1/_2$ to 2 hours. The accelerating quality of this rubber as a crude is maintained in compounded stocks—a fact which is not true for certain quick-curing plantation rubbers of the matured slab type. This accelerating property permits either an economy in compounding cost by virtue of a reduction in the amount of accelerator required, or a saving in curing cost if a shorter cure is desired.

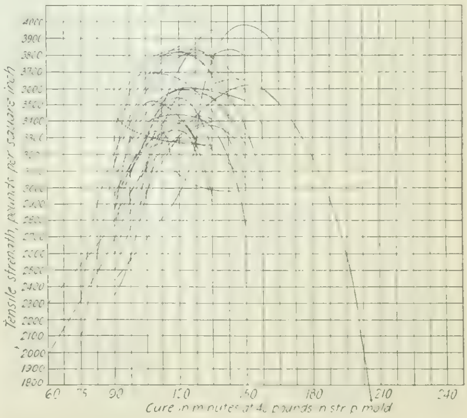


FIG. 2—TENSILE STRENGTH CURVES CONTROL TESTS ON SPRAYED RUBBER

The natural accelerator of vulcanization in LS rubber is present in the water-soluble nonrubber constituents. The exact identity of the various ingredients making up the nonrubber constituents has not been determined, but it is believed that some of these ingredients accelerate the rate of cure, some are neutral, and some may possibly have a retarding action on vulcanization.

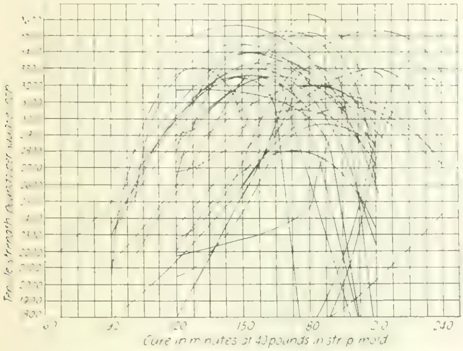


FIG. 3—TENSILE STRENGTH CURVES CONTROL TESTS ON SMOKED SHEET

From extensive tests made on LS rubber from which the water-soluble constituents were carefully removed, it was determined that the qualities of such prepared rubbers were inferior to the regular unwashed rubber, and for most purposes it is not considered desirable to remove these nonrubber constituents from commercial LS rubbers.

A tire-tread stock containing standard plantation crudes which cures in 105 minutes at 40 pounds in a mold will cure in about 75 minutes if LS rubber is used. In the case of an inner-tube compound the cure on the standard tube was reduced from 24 minutes to from 12 to 15 minutes by substituting LS rubber for the standard plantation crudes. Proportionate reductions in curing time have been noted in all cases where this rubber has been used. This quick-curing characteristic has not caused trouble with mill burning of stocks in the factories where a great many tons of LS rubber have been used in the production of standard products.

TABLE II—TYPICAL CURING RANGE OF EACH CRUDE 10 PER CENT SULFUR COMPOUND

(At 40 pounds pressure)

			Pale Crepe		
Time in Minutes	150	165	180	195	210
Tensile	2580	2970	3420	3310	2380
Stretch	10.4	10.4	10.1	9.8	8.6
Set	0.13	0.16	0.16	0.15	0.12
			Smoked Sheet		
Time in Minutes	120	150	165	180	210
Tensile	2680	3020	3365	2890	1140
Stretch	10.5	10.3	10.2	9.8	7.3
Set	0.14	0.17	0.17	0.16	0.07
			LS Rubber		
Time in Minutes	90	105	120	135	150
Tensile	3355	3740	3875	3570	3380
Stretch	10.3	10.2	10.0	9.8	9.5
Set	0.20	0.21	0.22	0.22	0.20
			Fine Para		
Time in Minutes	...	150	180	210	240
Tensile	...	2085	2730	3475	3475
Stretch	...	10.2	10.4	10.3	10.3
Set	...	0.14	0.16	0.17	0.22

AGING QUALITIES—Another valuable property of LS rubber is its good aging quality, it being very much superior to pale crepe and smoked sheet, and equal at least, if not superior, to fine Para. This improved aging quality is clearly apparent when accelerated aging tests are carried out on the crude compound with 10 per cent sulfur, and Table III gives data for such a test in comparison with crepe, sheet, and para.

TABLE III—AGING DATA

	TENSILE			STRETCH			SET		
	Under	Optimum	Over	Under	Optimum	Over	Under	Optimum	Over
Pale crepe	2750	3430	3080	10.4	10.1	8.6	0.13	0.16	0.12
Smoked sheet	2755	3350	3005	9.9	9.9	9.3	0.14	0.20	0.13
LS rubber	3335	3570	3265	9.7	9.8	9.3	0.16	0.20	0.23
Fine Para	2730	3475	3475	9.9	9.8	9.8	0.16	0.17	0.22
			1 Week's Heat Aging at 150° F.						
Pale crepe	3260	3215	2510	9.4	9.1	8.1	0.16	0.18	0.14
Smoked sheet	3080	3115	2605	8.8	8.6	8.2	0.14	0.18	0.15
LS rubber	3300	3145	3150	8.6	8.2	8.3	0.24	0.23	0.28
Fine Para	2765	2930	3215	10.1	9.7	9.2	0.15	0.15	0.18
			2 Weeks' Heat Aging at 150° F.						
Pale crepe	2140	1835	215	8.1	7.3	3.8	0.13	0.12	0.00
Smoked sheet	1725	1230	330	7.5	6.3	3.8	0.10	0.07	0.00
LS rubber	2660	2660	2495	8.1	7.6	7.3	0.16	0.22	0.21
Fine Para	2030	2685	2335	8.9	8.7	7.9	0.14	0.16	0.15
			3 Weeks' Heat Aging at 150° F.						
Pale crepe	160	135	104	2.7	2.1	2.0	0.00	0.00	0.00
Smoked sheet	135	230	135	2.3	2.1	2.1	0.00	0.00	0.00
LS rubber	1260	450	390	6.0	3.5	3.5	0.08	0.02	0.00
Fine Para	162	225	155	3.8	3.7	2.4	0.00	0.00	0.00

Each stock was given a range of three cures, the first being under, the second being the optimum and the third being over. The optimum tensile was taken as the optimum cure. The cures are as follows:

TIME IN MINUTES AT 40 POUNDS PRESSURE

	Under	Optimum	Over
Pale crepe	150	180	210
Smoked sheet	150	180	210
LS rubber	105	120	135
Fine Para	180	210	240

All rubbers were cured with 10 parts of sulfur on 100 parts of rubber.

Shelf aging tests covering a period of three years have checked the accelerated aging tests, and demonstrate beyond all doubt that this rubber has unusual aging qualities in cured goods. This quality may be due to both the protective action of the nonrubber constituents present and to the method of preparation.

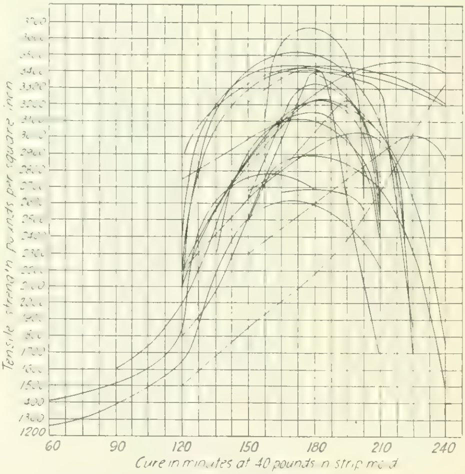


FIG. 4—TENSILE STRENGTH CURVES CONTROL TESTS ON PALE CREPE

APPLICATION

LS rubber has been used in tire treads, carcass compounds, inner tubes, soles, heels, belt covers, cements, and rubber goods generally, and because of its superior qualities of uniformity, aging, high strength, and quick cure, it has a wide and rapidly growing application.

Annual inspection of the mineral wells and springs in Kentucky, Tennessee, Mississippi, Texas, Arkansas, and Missouri that ship water into interstate commerce has been completed by the Bureau of Chemistry, over 100 commercial wells having been visited. Improvement in the sanitary conditions about the wells and springs and in methods of bottling the water was noted in various places.

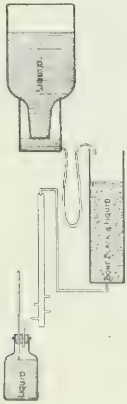
Automatic Char-Filtration Apparatus[1]

By W. D. Horne and E. W. Rice

National Sugar Refinery, Yonkers, N. Y.

IN COMPARING the values of samples of bone black for sugar filtration it is customary to run comparative filtration tests. Similar filtration experiments are of great practical value in comparing some of the properties of sugars themselves, as well as varying methods of treatment. Thus, the effects of the reaction of the solution, its time of contact, concentration, temperature, the ratio of char to sugar solids, the shape and proportions of the filter, the depth of char, and other factors are all occasionally to be considered.

In applying these tests it is desirable that the conditions be such that results obtained experimentally on a small scale shall be interpretable as far as possible into refinery practice on a working scale. Among the house conditions required to be simulated in the laboratory, that of length of time of contact has been one of the most inconvenient ones to arrange, as the bone black in refinery practice is usually in contact with flowing sugar solution for many hours, and a laboratory test, to be most accurate, should provide this feature as well as others. Hence the need of some automatic device to feed a sugar solution steadily upon the char, to draw it off with sufficient regularity, and to segregate the successive portions of the filtrate in individual containers. It is the purpose of this paper to describe such a device, as briefly as possible, omitting details of the various trials leading up to the satisfactory accomplishment.



The apparatus devised consists of three main divisions. The central feature is a set of copper tubes properly held in a vertical position in a water bath, the temperature of which is regulated by a thermostat. The filter tubes for containing char have smaller bottom tubes passing through the bottom of the bath which are provided with cocks. There is a wire gauze in the bottom of each filter, overlaid by a disk of cloth. The determined amount of char (a few hundred grams) having been placed in the filter, the determined number of grams of sugar solids in solution are run through the char in the required time.

If the size of the filter is to be kept within convenient dimensions, a rate of flow which is so slow as to be difficult to provide in any ordinary manner is sometimes necessary. This difficulty is met by the second part of the apparatus, the feeding device. The feed is accomplished by a cylindrical container in the top of which is an inverted bottle containing the sugar solution to be used. This provides a reasonably constant head of the liquid in the cylinder, for the solution flows out of the bottle into the cylinder until it rises high enough to close the end of the feed tube, after which the level is automatically controlled to within about 1.5 mm. while the bottle is nearly full, and to within about 5 mm. when it is nearly empty.

These slight variations of head are negligible, for, while they may cause a very small variation in rate of flow as between the moments before and after any individual delivery of solution from the bottle to the cylinder, the rate of flow considered as a whole remains constant. From the bottom of the cylinder runs a small, rubber feed pipe connected with a fine copper tube 35 cm. long and of 1.5 mm. internal diameter, forming a gooseneck, the top level of which is carefully set in reference to the level of the liquid in the cylinder so as to give the required hydrostatic head and rate of flow. The long, narrow tube is essential to produce enough frictional resistance to allow an appreciable head for the solution in the cylinder. From the gooseneck the solution drips very slowly into a glass tube leading into the filter.

It would be simpler, were it practicable, to feed from an inverted bottle directly into the char filter, and regulate the rate of flow by adjusting the level of the gooseneck tube leading to the distributing device, but it has been found that, owing to the disengagement of air from the char or other causes, a very slow constant rate of flow through the char could not be maintained. By having the independent feed described above, the level of the liquid will rise in the filter, if the flow ceases, until the increased head sets the flow into operation again.

The third part of the apparatus is the distributor which properly cares for the char filtrate. After the dripping liquid has gradually filled up the filter to a point a little above the char level, the filtered solution begins to overflow through an external tube and gooseneck into the distributing device.

The distributor is a brass tube about 30 cm. long and of 6 mm. inside diameter attached vertically by a clamp to the outside of the water bath that holds the filters, and has at its lower end a series of 1.5-mm., short metal tubes radiating from it at differences in height of about 1 cm. The filtrate dripping into the brass tube flows slowly out of the lowest of these radiating tubes into a 100-cc. bottle. The neck of this bottle is closed by a stopper through which passes a fine brass tube that connects very closely end to end with the lowest radiant tube by means of rubber tubing. Through the collecting stopper passes vertically a second brass tube 10 cm. long, the lower end of which stands at the level where the filtrate is to be stopped. When the first collecting bottle becomes full, the filtered solution from the char collects in the vertical brass distributing tube until its level rises 1 cm. when it begins to flow into the second collecting bottle. This operation continues through the cycle of as many bottles as desired. In order to insure certain passage of the filtered liquor through these fine tubes leading to the bottles, it is well at the assembling of this part of the apparatus to moisten the inside of the various single tubes with water to decrease resistance to the first flow of sugar solution. Care should be taken, however, that the air outlet tubes from the bottles contain no drops of water to cause back pressure.

Effect of Sea Water on Glass

The Bureau of Standards has conducted an investigation on the effect of sea water on various types of glass to determine the best kind to use for the lenses of signal lights on ship board. From the data secured, the damage which these lenses often suffer appears to be caused by the evaporation of sea spray, which leaves a deposit of salt on the surface of the lens. This eventually etches the glass. Three types of glass—borosilicate, lead glass, and ordinary soda-lime glass—have been investigated. Under the conditions of the test, lead glass etched considerably, while the other two did not.

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[1] Presented before the Division of Sugar Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

The Oxidation of Ferrous Sulfate to Ferric Sulfate by Means of Air[1]

By J. H. Reedy and J. S. Machin

University of Illinois, Urbana, Ill.

The conversion of ferrous sulfate into ferric sulfate takes on practical importance in the Rio Tinto process for extracting copper from poor pyritic ores, in which ferric sulfate solution is used as the leaching agent. Jones[2] has represented the fundamental reactions involved as follows:

$$Cu_2S + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 2FeSO_4 + CuS \text{ and}$$
$$CuS + Fe_2(SO_4)_3 + 3O + H_2O \longrightarrow CuSO_4 + 2FeSO_4 + H_2SO_4$$

The copper is precipitated from the leaching solution by scrap iron, and if the ferrous sulfate formed could be readily oxidized to ferric sulfate, this process might be made cyclic and continuous, resulting in a great saving of time and material.

Contrary to popular opinion, ferrous sulfate cannot be completely oxidized to ferric sulfate very readily by means of air, notwithstanding the fact that the reaction is highly exothermic and for this reason might be expected to proceed rapidly. Experiment shows that the reaction velocity falls off very rapidly, and a surprisingly long time is required for complete oxidation.

Various attempts have been made to develop methods for the regeneration of ferric sulfate from the reduced salt. Notable in this respect is the method of Austin,[3] in which a blast of air was forced into a hot solution of ferrous sulfate. An efficiency of only 58 per cent was attained, and a considerable amount of iron was precipitated as basic sulfate unless a certain amount of free sulfuric acid was present. This incomplete oxidation is very unsatisfactory, for Thomas[4] has shown that the presence of ferrous sulfate hinders the solvent action of ferric sulfate on copper sulfide. Other ways of bringing about this oxidation have been tried, but with poor results.

Following is a brief account of the results of a study of the conditions which influence the speed of this reaction.

Effect of Concentration and Temperature

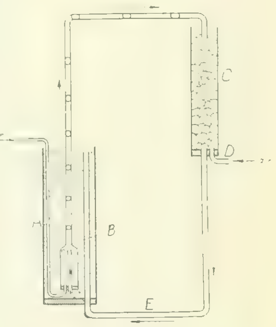
Solutions of ferrous sulfate of strengths ranging from 2 to 7 per cent by weight (calculated as the anhydrous salt) were aerated by bubbling air through them. The amount of free acid was varied from zero to about 5 per cent, and temperatures of 25°, 55°, 80°, and 95° C. were used. These tests showed that the concentration of the ferrous sulfate makes little difference in the velocity of the reaction, that the reaction proceeds somewhat better in neutral than in acid solutions, and that the speed of the reaction is greatly increased at higher temperatures. In neutral solutions basic salts were precipitated. The composition of this precipitate seemed to be unaffected by change in temperature, a representative analysis showing 68.95 per cent iron, 9.71 per cent sulfate, and 21.34 per cent (by difference) hydrogen and oxygen. This composition indicates a mixture of substances, presumably basic ferric sulfate and colloidal ferric hydroxide.

Sulfur Dioxide as a Source of Sulfuric Acid

It has been suggested that the free sulfuric acid required to prevent the formation of basic salts might be obtained from the sulfur dioxide in stack fumes. Air containing sulfur dioxide was passed through a tube containing ferric oxide at 550° C., and the product passed directly into ferrous sulfate solution. It was found, however, that the oxidation of sulfur dioxide to sulfuric acid was not complete unless the concentration of the sulfur dioxide was very low (about 0.5 per cent by volume), and that the unchanged sulfur dioxide, by its reducing action, prevented the oxidation of ferrous sulfate to ferric sulfate. When, however, the amount of sulfur dioxide was sufficiently low, the oxidation proceeded slowly without the formation of any basic salt.

Catalytic Effects

The foregoing results suggest that this reaction might be made to run more smoothly under the influence of the proper catalyst. Manganese dioxide seemed to be the most likely contact agent, since the oxides of the other metals showing multiple valences—e. g., cobalt, lead, copper, etc.—are soluble in dilute sulfuric acid and would be leached out in a very short time.



After trying other devices, a continuous automatic method in which the solution was made to circulate cyclically through a tower containing the catalyst was devised. The apparatus is represented diagrammatically in the figure. The cylinder *A* contains the ferrous sulfate solution to be oxidized. A blast of air is passed into the tube *B*, and a mixture of the solution and air bubbles is carried over into the tower *C* containing the catalyst. A countercurrent of air is introduced into the bottom of the tower at *D*, and the oxidized solution is returned to *A* by means of the tube *E*. In the first runs made, the catalyzing tower was charged with pumice stone covered with pure manganese dioxide, prepared by the reduction of potassium permanganate. This procedure was unsatisfactory, however, since the manganese dioxide washed off easily, and seemed to become coated over with a deposit of basic ferric sulfate.

Native manganese dioxide (pyrolusite) was next tried. The catalyzing tower was filled with pieces about 1 cm. in size, and a normal solution of ferrous sulfate containing the theoretical amount of sulfuric acid for the formation of the normal ferric sulfate was used. The solution was run into the top of the tower at the rate of 100 cc. per minute. After all the solution had passed through once, a test showed that 82 per cent of the iron had been oxidized to the ferric condi-

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[1] Received July 13, 1923.

[2] *Trans. Am Inst Mining Met. Eng.*, **35**, 3 (1905); *Mineral Ind*, **12**, 112 (1903).

[3] "Mines and Methods," September, **1910**; Greenwalt, "Hydrometallurgy of Copper," **1912**, p. 194.

[4] *Metallurgie*, **1**, 59 (1904).

tion. The oxidation was complete after passing the solution through the tower five times. Equally satisfactory results were obtained with other concentrations of ferrous sulfate solution. All these runs were made at room temperature. Neutral solutions of ferrous sulfate gave considerable amounts of the basic sulfate, covering the catalyst, especially where the pieces touched each other or the walls of the tower. Using solutions containing the theoretical amount of acid, only little basic sulfate was formed, and this did not appear to reduce the efficiency of the process appreciably. The catalyst is easily cleaned without removing it from the tower by washing with a little dilute sulfuric acid.

The same lot of manganese dioxide was used for all the runs made and during these experiments showed no tendency toward becoming "poisoned" or otherwise losing its efficiency. The pyrolusite used showed on analysis the usual impurities common to the mineral—iron, silica, etc. It is very interesting to note that, while this impure substance was wonderfully active as a catalyst, the pure material had very little action.

Analysis of Mixed Salts by Freezing Point Method[1]

By Howard E. Batsford

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ANALYSIS by freezing point method has been practiced in isolated cases for some time, and can be used to good advantage in a plant where mixtures of fairly pure, simple salts are encountered.

So-called freezing point curves of various salt mixtures in which binary, ternary, and quaternary mixtures are involved have been mentioned in the literature. From German literature the triangular method of plotting the ternary mixtures used in this article is obtained.

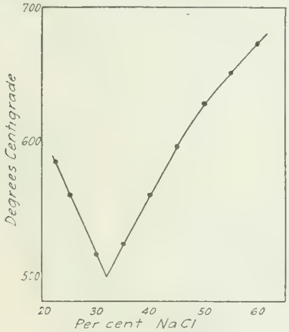

Fig. 1—Freezing Point Curve of NaCl–$CaCl_2$ Mixtures

In 1920 Lautsberry and Page[2] published the results of their search for simple mixtures of molten salts suitable for steel treatment. They used sodium, calcium, and potassium chlorides, and arrived at the following data:

1—With sodium and potassium the minimum freezing point is 650° C. for 55 per cent potassium chloride.

2—With calcium and sodium chlorides the minimum freezing point is 505° C. for 72.5 per cent calcium chloride.

3—With calcium and potassium chlorides two eutectics and a maximum point were obtained. The maximum freezing point is 725° C. for $2KCl.3CaCl_2$. The two eutectics are 608° C. with 17.5 per cent potassium chloride, and 590° C. with 60 per cent potassium chloride.

4—With potassium, sodium, and calcium chlorides two eutectics were obtained—namely, 495° C. for 70 per cent calcium chloride, 25 per cent sodium chloride, and 5 per cent potassium chloride; 530° C. for 30 per cent calcium chloride, 20 per cent sodium chloride, and 50 per cent potassium chloride.

These results show in large print in the plot of ternary mixtures (Fig. 2).

In order to prepare for such analyses in plant control work, a series of salt mixtures should be prepared and analyzed and then used for freezing point determination, thus yielding a freezing point curve which will be a great time saver to the chemist or plant control man.

Such plots have been prepared in the case of sodium and calcium chlorides, and mixtures of sodium, calcium, and potassium chlorides, and are shown with proper explanation of their use in analysis.

The ordinary method of routine analysis of salt mixtures consists in getting the percentage of calcium and chlorine and estimating the sodium by difference. By use of the curve shown in Fig. 1 the analysis is easily obtained by running the calcium volumetrically with standard oxalic acid and determining the freezing point. For instance, let us assume a salt mixture containing 15.63 per cent calcium and having a freezing point of 660° C. There are two mixtures with this freezing point, but only one answering to the calcium analysis—namely, 56.65 per cent sodium chloride and 43.35 per cent calcium chloride.

Fig. 2 shows the type of curve plot used with ternary mixtures of salts. Here the plot is in the form of a triangle with the pure salt at each corner and various diminishing percentages represented by parallel lines at regular distances from the corner. Thus, the top point of the triangle stands for 100 per cent potassium chloride and the line connecting the other two corners is zero per cent potassium chloride. The curves shown are isotherms, or lines extending through various mixtures having the same freezing point. The mixture having the lowest freezing point is called the eutectic and in this plot is of practically constant sodium chloride content for a change of 30 per cent calcium and potassium chlorides.

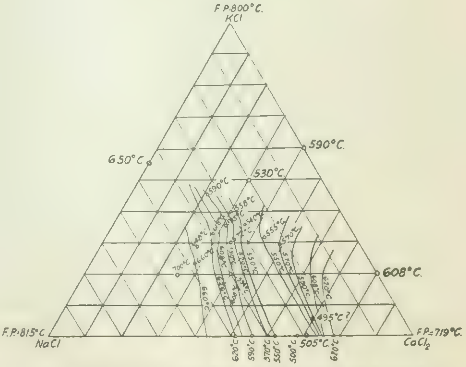

Fig. 2—Freezing Points of Mixtures of NaCl, $CaCl_2$, and KCl

Let us assume the analysis of a mixture of these three salts yields the following:

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[1] Received May 21, 1923.

[2] *J. Soc. Chem. Ind.*, **39**, 37 (1920).

Calcium, 14.43 per cent, equivalent to 40.00 per cent $CaCl_2$; freezing point, 620° C.

By consulting Fig. 2 at the proper freezing point the mixture is found to consist of 40 per cent calcium chloride, 46 per cent sodium chloride, and 14 per cent potassium chloride.

These and similar curves are also very useful for the reverse operation—namely, the determination of freezing points of various salt mixtures, especially in connection with the operation of the so-called fused electrolyte furnaces. A very close control can be kept on the feeding of these furnaces by a systematic follow-up of freezing points.

The usual procedure of freezing point determination is to fill a small iron crucible with molten salt mixture, suspend in it a base-metal thermocouple, and record the temperature or freezing point curve on a suitable graphic instrument. Just before complete solidification the couple may be withdrawn from the salt and washed in readiness for the next determination.

The Vapor Pressures of Gasolines and Light Petroleum Naphthas[1]

By **F. H. Rhodes** and **E. B. McConnell**

CORNELL UNIVERSITY, ITHACA, N. Y.

A method for the exact determination of the vapor pressures of gasoline and naphthas is described, and the vapor pressures of several different types of gasolines and naphthas are measured.

It is shown that no general relation exists between the vapor pressure of a gasoline and its average distillation temperature or its density, and that the presence of air dissolved in the gasoline or naphtha may introduce into the vapor pressure determination an error of considerable magnitude.

UPON the vapor pressure exerted by a gasoline or a light petroleum naphtha at or slightly above the ordinary temperatures depend, to a considerable extent, the loss which will be incurred when the material is handled or stored, the internal pressure developed in shipping containers used for transporting the material, the fire hazard incurred in handling the naphthas, and the ease with which the gasoline may be vaporized in the carburetor of an internal combustion engine.

A number of methods for the determination of the vapor pressure of gasoline have been devised, and some information on the vapor pressures of gasolines has been published. The method commonly used for testing casinghead gasolines and blended gasolines in order to determine whether or not they may safely be shipped in tank cars or standard drums, has been described by the U. S. Bureau of Explosives.[2] A steel bomb is partially filled with the naphtha to be tested, the bomb and its contents are heated to the temperature at which the determination is to be made, and the pressure within the bomb is observed. In order to decrease the error due to the expansion of the air in the space above the liquid, this space is momentarily vented to the atmosphere when the temperature of the gasoline reaches 70° F.

This method is subject to several sources of error. Some of the lighter components of the gasoline may be vaporized below 70° F., and the vapors thus formed will escape when the relief valve is opened to vent the expanded air. When the bomb is heated from 70° F. to the temperature at which the vapor pressure is to be measured (90° or 100° F.), the air above the liquid tends to expand, and the increase in pressure thus developed is measured with and not differentiated from the increase due to the true vapor pressure of the gasoline. Some of the air present in solution in the original sample may be liberated when the naphtha is warmed, and the pressure developed by this liberated air may be measured along with the true vapor pressure. No means for agitating the liquid is provided so that there is no assurance that the liquid and the vapor within the bomb are in true equilibrium with each other. A modification of this bomb has been devised[3] whereby some of these errors are eliminated. This improved method is, however, still subject to the error due to the presence of air dissolved in the gasoline. The results obtained by these methods, while they may be of value in estimating the pressures developed in shipping containers, do not give the true vapor pressures of the naphthas.

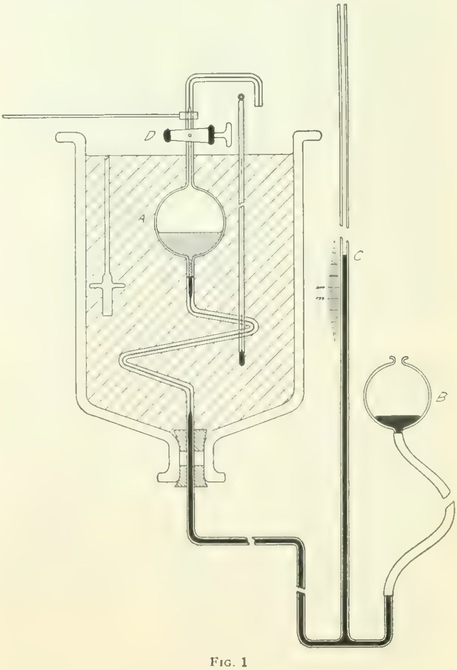

FIG. 1

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[1] Received June 20, 1923.

[2] Report of Chief Inspector of Bureau of Safe Transportation of Explosives and Other Dangerous Articles, February, **1916**.

[3] Private communication from R. P. Anderson.

The relations which exist between the vapor pressure of a gasoline at a given temperature and the other characteristics of the gasoline have been studied by a number of investigators. Obviously, a gasoline with a low average distillation temperature should show a relatively high vapor pressure. Wiggins[4] states that with the lighter fractions from midcontinent crudes the vapor pressures vary as the Baumé gravity. This relationship holds true, of course, only when comparing fractions from crudes of similar types.

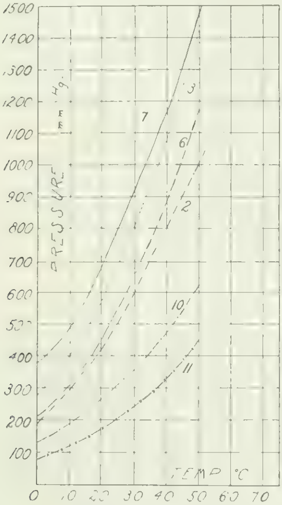

FIG. 2

The investigation described in this present article was undertaken for the purpose of determining the true vapor pressures, at moderate temperatures, of gasolines and naphthas of various types. Incidentally, an attempt has been made to derive some correlation between the vapor pressures of various gasolines at a given temperature and some of the other characteristics of the gasolines.

APPARATUS

The apparatus used in this work was a modified form of the apparatus described by Browne and Houlehan[5] and by Richardson,[6] and which has been used by Browne and his coworkers in various investigations. (Fig. 1) A glass bulb of approximately 40 cc. capacity was mounted in a water bath and was connected, through a spiral of capillary glass tubing, with a mercury-filled manometer, *C*. The bulb was attached to an arm, which was connected to an eccentric so that the bulb and its contents could be shaken vigorously. A fixed zero point was marked on the tube just below the bottom of the bulb. The corresponding zero point on the manometer—i. e., the point at which the mercury stood in the manometer when the mercury in the bulb was at the zero point and when both sides of the mercury column were under atmospheric pressure—was also marked. The corrections to be applied to the zero reading on the manometer to compensate for differences between the temperature of the mercury in the manometer and the temperature of the mercury in the spiral within the thermostat were also determined.

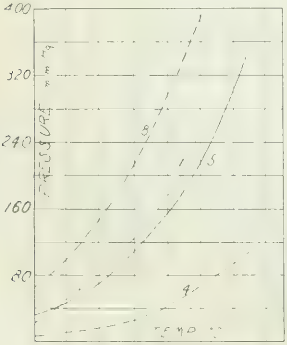

FIG. 3

PROCEDURE

All the air was forced out of the bulb *A;* then about 15 cc. of the sample were drawn into the apparatus. After closing the stopcock *D*, the leveling bulb *B* was lowered until the gasoline began to boil vigorously under the reduced pressure. The leveling bulb was then raised until the sample was under slightly greater than atmospheric pressure. The vapor recondensed and redissolved in the liquid, but any air which had been liberated during the boiling-out process remained unabsorbed and could be removed by opening the stopcock above. This cycle of boiling, recondensation, and removal of the liberated air was continued until no more air was set free—i. e., until the vapor recondensed completely when the pressure was raised.

After the removal of the dissolved air the water in the thermostat was brought to the exact temperature at which the determination was to be made. The leveling bulb was lowered until the mercury within the apparatus stood at the zero point. The bulb was shaken vigorously to establish equilibrium between liquid and vapor and to insure that the liquid and vapor within the bulb were at the same temperature as the water within the thermostat. The leveling bulb was adjusted from time to time to keep the level of the mercury at the zero point. The agitation was continued for several minutes after there was no further change in the level of the mercury. The reading of the manometer was then taken, and from the barometric pressure and the difference between the manometer reading and the zero point on the manometer the vapor pressure of the gasoline at the temperature of the thermostat was calculated. (All manometer readings were, of course, corrected for the difference between the temperature of the column of mercury within the thermostat, and for the weight of the layer of gasoline above the mercury within the bulb.)

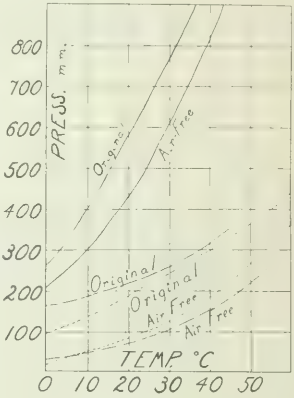

FIG. 4

TESTS FOR ACCURACY OF METHOD

In order to determine the accuracy of this method of determining vapor pressures, a series of runs was made using pure water at various temperatures. The results obtained agreed to within 1 mm. with those given by Regnault.

The gasolines and naphthas which were examined were as follows:

SAMPLE	DESCRIPTION
1	Straight-run petroleum naphtha. Pennsylvania Oil Co., used for blending with casinghead gasoline
2	Absorption (casinghead) gasoline from the Pennsylvania Oil Co.
3	Blended gasoline, from absorption gasoline, from the Pennsylvania Oil Co.
4	Crude naphtha fraction, from paraffin-base oil, from the Conewango Refining Co.
5	Crude gasoline fraction, from paraffin-base oil, from the Conewango Refining Co.
6	Absorption gasoline from the Mars Co.
7	Absorption gasoline from the Mars Co.
8	Motor gasoline (Texaco) purchased on the market
9	Motor gasoline (Socony) purchased on the market
10	Special gasoline from the Atlantic Refining Co.
11	Special gasoline from the Atlantic Refining Co.

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[4] *Oil Gas J.*, **19**, 42, 568 (1921).

[5] *J. Am. Chem. Soc.*, **35**, 649 (1913).

[6] *Ibid.*, **39**, 1828 (1917).

Table I—Vapor Pressures of Gasolines and Naphthas

Sample	1	2	3	4	5	6	7	8	9	10	11
Specific gravity at 15.5° C.	0.764	0.672	0.679	0.763	0.733	0.664	0.670	0.744	0.743	0.731	0.723
Degrees Baumé at 15.5° C.	53.2	78.3	76.2	53.5	61.0	80.8	79.0	58.2	58.4	61.5	63.6
Size of Sample				Distillation Temperature ° F.							
Cc.						Start					
	62	26	25	104	65	30	24	42	40	29	59
10	115	43	36	124	85	38	42	75	75	79	78
20	132	52	44	131	91	43	51	90	94	101	91
30	145	61	53	137	97	46	60	106	105	116	99
40	153	70	64	145	103	50	68	112	115	129	105
50	160	79	86	152	107	55	78	135	125	133	112
60	168	90	111	160	112	62	89	146	135	152	116
70	175	100	144	169	117	76	98	155	146	161	129
80	185	119	191	182	126	88	118	167	162	175	140
90	202	. . .	. . .	201	144	111		190	182	204	159
Dry	218	167	212	237	175	141	163	221	215	217	194

The density (at 15.5° C.) and the distillation range of each of these samples were determined following the procedure described in Bureau of Mines *Technical Paper* **298** (1922). The results are shown in Table I.

The vapor pressures of the various gasolines and naphthas (air-free) were determined. The results are shown in Figs. 2 and 3.

ERROR CAUSED BY DISSOLVED AIR

A few experiments were also made to determine the approximate magnitude of the error which may be introduced by the presence of air in solution in the gasoline. Samples of the original gasolines were introduced into apparatus and their vapor pressures were determined before removing the dissolved air. The air was then boiled out as described above, and the vapor pressure of the air-free material was determined. The results are shown in Fig. 4. It will be observed that the presence of the dissolved air introduced a very considerable error. The exact magnitude of the error from this source will depend, in any specific case, upon the amount of air present, the nature of the gasoline, and the method by which the vapor pressure is determined.

RELATION BETWEEN DENSITIES AND VAPOR PRESSURES

The relation between the densities (at 15.5° C.) and the vapor pressures (at 20° C. and 40° C.) of the various gasolines and naphthas is shown by Fig. 5. It will be observed that, in general, the samples with the lower densities show the higher vapor pressures. In most cases there appears to be a rather definite relation between the density and the vapor pressure at any given temperature. Some of the samples, particularly some of those containing casinghead gasoline, show abnormally high vapor pressures, while the sample of crude naphtha fraction (Sample 4) showed abnormally low vapor pressures. It is evident that the vapor pressure cannot in every case be predicted, even approximately, from the density.

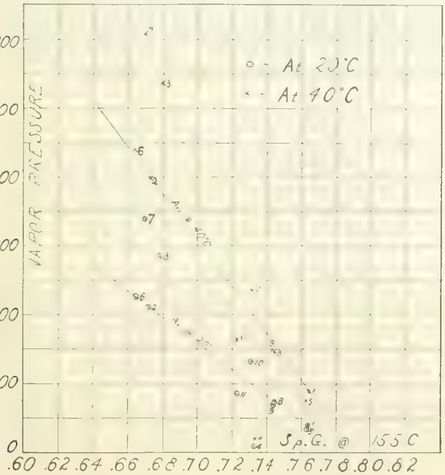
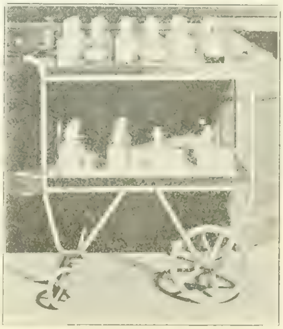


Fig. 5

RELATION BETWEEN DISTILLATION TEMPERATURES AND VAPOR PRESSURES

From a comparison of the data for the distillation ranges and the vapor pressures of the various samples it will be noted that, as might be expected, the samples with a relatively low average distillation temperature show relatively high vapor pressures, and vice versa. The relation between distillation temperatures and vapor pressures is, however, not sufficiently definite and uniform to permit the accurate prediction of the vapor pressure from the distillation data.

Portable Desk and Reagent Carrier



The accompanying illustrations show two unique conveniences several of which are in use in Lehn & Fink's laboratory—a portable desk and chair and a tea-wagon reagent carrier. The desk is adjustable and contains a drawer for notebooks, etc. The tea wagon offers a convenient and quick means of having at hand a set of reagents at any particular place in the laboratory where the chemist happens to be working.

Notes on the Oil from Kauri Copal[1]

By Augustus H. Gill and D. Nishida

Massachusetts Institute of Technology, Cambridge, Mass.

FOR varnish-making by the American method gum copal is heated over an open coke fire at a temperature of about 330° C. until from 10 to 25 per cent is driven off up the chimney. By the English process a cover arranged with a condensing outfit connected to suction is used. This collects much of the oil, which is known as copal oil. It has been used to mix with turpentine, but it does not give good results on paint and varnish films. According to Vaubel[2] it can be detected in the turpentine residue by its odor and bromine number.

Other investigators report as follows:

Scheibler[3] subjected "copal from Manila" to dry distillation and noted two distinct stages in the process, but has nothing to say about the composition of the distillate.

Tschirch[4] states that the dry distillation of hard copal yields formic, acetic, and succinic acids among the products of the decomposition.

Friedburg[5] noticed that certain copals yielded a distillate having an odor suggestive of limonene, but he was unable to isolate the latter, and he did not state what variety of copal had this property.

Wallach[6] subjected kauri copal to destructive distillation and succeeded in isolating pinene and dipentene, but said nothing about the quantities of them.

Guedras[7] also reported almost the same result as that obtained by Wallach.

Neither the results obtained by Wallach or Guedras, however, are obtained from the technical kauri copal oil, but from the laboratory products.

Schmölling[8] examined kauri and manila copal oils, which are obtained technically in varnish-making, and found that they are soluble in the usual organic solvents except petroleum ether, and that they have the following characteristics:

	Kauri Copal	Manila Copal
Specific gravity (15° C.)	0.8677	0.9069
Acid value, mg. KOH	3.0	28.3
Saponification value, mg. KOH	4.9	45.7
Ester value	1.9	17.4
Iodine value	288.9	230.4

RESULTS OF FRACTIONATION

	Kauri Copal		Manila Copal	
Fraction	Temperature ° C.	Per cent	Temperature ° C.	Per cent
I	125 to 155	21.0	To 155	26.0
II	155 to 157	38.5	155 to 165	26.0
III	157 to 170	24.7	165 to 170	12.3
IV	Over 170	15.8	....	....

From the Fraction II of kauri copal oil he obtained much crystalline pinene nitrosochloride; he also found from Fraction IV limonene-like substances, but no other terpenes, nor any of their characteristic derivatives, were isolated. The aqueous portion of the distillate gave reactions for formic and acetic acids.

RESULTS OF PRESENT STUDY

The sample used for this examination was a by-product of varnish-making with kauri copal and had the commercial name "Gum Spirits." It was a dark yellow, viscous liquid, almost insoluble in water, but very soluble in 96 per cent alcohol, glacial acetic acid, ether, chloroform, carbon bisulfide, carbon tetrachloride, benzene, and petroleum spirit. When the oil was spread out on a glass plate in thin layers and exposed to the air, it gradually solidified and a resinous film was produced within 5 or 6 days. The oil had the following characteristics:

Specific gravity, at 20° C.	0.9667
Flashing point, by Pensky-Marten tester	85° to 86° C.
Specific rotation, $[\alpha]_D^{20}$	+3°, 40′
Specific viscosity, at 20° C., Engler	11.8
Refractive index, at 25° C.	1.5128
Acid value (free acid), mg. KOH	69.0
Saponification value	83.0
Iodine value, by Hanus method, 15 minutes	114.0

The raw oil was treated with 10 per cent potassium hydroxide solution to remove acids, washed with water, dehydrated with anhydrous sodium sulfate, and by distilling it under diminished pressure a straw-yellow colored transparent oil was obtained, giving a yield of 52 per cent. The refined oil thus obtained had the following characteristics:

Specific gravity at 20° C.	0.9280
Specific rotation $[\alpha]_D^{20}$	+2°, 46′
Specific viscosity at 20° C., Engler	1.7
Refractive index at 25° C.	1.5102
Iodine value, by Hanus method, 15 minutes	104.0

The refined oil had the same drying property as the raw oil and gave the color reactions of rosin oil with the Lieberman starch test.

When distilled under 15 to 16 mm. pressure the following fractions were obtained:

Fraction	Temperature ° C.	Per cent
I	Up to 120	4.3
II	120 to 200	53.0
III	200 to 250	41.3
Residue	....	1.4

These figures are quite different from those described by Schmölling.

Fraction I was a slightly yellow-colored liquid closely resembling turpentine as regards its odor, specific gravity, refractive index, and rotation; it was fractionated at atmospheric pressure at temperatures up to 165° C., 165° to 180° C., and 180° to 200° C. About half of it came over at the middle temperatures. Pinene was found in Fraction I and limonene in Fractions II and III, using Wallach's[9] method of the nitrosochlorides. No aldehydes or ketones could be identified by the bisulfite method.

Fraction II had characteristics suggesting sesquiterpenes, such as boiling point, specific gravity, etc., but the fact that the fraction formed no crystalline compounds with amyl nitrite or with dry hydrochloric acid[10] would seem to show there are no sesquiterpenes contained in this fraction.

Fraction III closely resembled diterpenes or polyterpenes by its boiling point, specific gravity, and fluorescence, or these characters are almost the same as those of colophene and diterpilene, but the chemical characteristics of both colophene and diterpilene have been little studied; therefore no methods for exact identification have been obtained.

Schultze[11] had treated ordinary rosin oil with concentrated sulfuric acid and obtained saturated hydrocarbons with the yield of 36 per cent of refined rosin oil, in which he found

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[1] Received July 10, 1923.

[2] *Z. angew. Chem.*, **33**, 1165 (1920).

[3] *Ann.*, **113**, 338 (1860).

[4] *Arch. Pharm.*, **240**, 202 (1902).

[5] *J. Am. Chem. Soc.*, **22**, 285 (1890).

[6] *Ann.*, **271**, 380 (1892).

[7] *Chem. Ztg.*, **26**, 1132 (1902)

[8] *Ibid.*, **29**, 955 (1905).

[9] *Ann.*, **245**, 241 (1888).

[10] Allen, "Commercial Organic Analysis," Vol. IV, p. 186.

[11] *Ann.*, **359**, 129 (1908).

octahydroretene, and confirmed this by treating the saturated oil with sulfur with which octahydroretene was dehydrogenated, and obtained crystals of retene.

Experiments were carried out following Schultze's directions. At first the mixture of Fractions II and III was treated with concentrated sulfuric acid, and saturated compounds were obtained, with a yield of about 19 per cent of the refined oil. This saturated kauri copal oil has some resemblance to the saturated resin oil which has been described by Schultze, but is quite a different substance because it gives neither retene by treating with sulfur, nor trimellitic acid by oxidizing with dilute sulfuric acid and manganese dioxide; therefore, in order to confirm this composition some other method is necessary.

Nothing was learned by treatment with nitric acid or oxidation with alkaline permanganate.

A New Method of Gas Analysis[1]

By **Rudolph Geberth**

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TO OVERCOME objections to the chemical methods of making quantitative determinations of gases, as employed by the manufacturers of commercially used gases, an apparatus has been designed by Samuel Ruben, a physicist of New York, based upon principles of resonance, by which such determinations as to binary gases are made with great accuracy and speed.

Broadly considered, the apparatus involves the principle that mechanical energy impulses, such as sound waves, produced by a vibrating element, differ in character with the condition of the gas through which they are transmitted. By "condition" is meant either a physical property, as density, or its chemical composition.

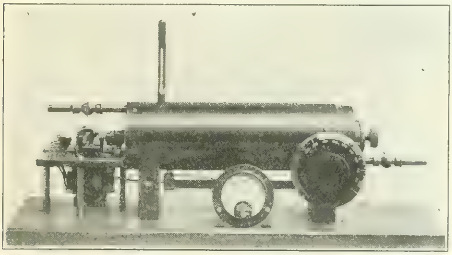

Fig. 1—Apparatus for Gas Analysis

The accompanying illustration (Fig. 1) shows the complete apparatus, consisting of a closed cylinder, adjustable as to length, through which the gases are passed, and having at one end a diaphragm coupled to a tuning fork, electrically maintained, together with a current-measuring instrument. One of the cylinders is closely movable within the other by means of a rack and gear arrangement, and has a graduated dial attached to the gear shaft for indicating gas column length. A thermometer projects into the chamber for temperature corrections.

The tuning fork is oscillated at a constant rate by an electromagnet having a carbon transmitter as a variable resistance. As the column is brought close to the resonance point, the ammeter, in series with the electromagnet, indicates a very sharp current rise. The input current of the driving element depends upon the amplitude of the fork vibration as controlled by the diaphragm, its force of reaction against the fork varying according to the condition of the gas in respect to its resonance length.

When the column is in resonance with the sound wave length, the load upon the fork is at a maximum and is sharply so indicated by the ammeter. The dial reading, then, which is in accord with that of the ammeter, indicates the resonance length of the gas column. The accompanying curve shows the relation between the length of chamber and the ammeter readings. (Fig. 2)

The resonance length of a known gas is indicated by the relation between the velocity and the frequency of sound through that gas; or the resonance length L is equal to the wave length λ of the sound source.

$$\lambda = \frac{V}{f};\ \lambda = L$$

$$V_0 = \sqrt{1.4\frac{p}{d}}\,;\ V_t = \sqrt{1.4\frac{p}{d}\,(1 + at)}\,;\ V_t = V_0\sqrt{1 + at}$$

where p equals pressure; d, density; a, temperature expansion coefficient, 0.003665; t, operating temperature; V_0, velocity at ° C.; f, frequency.

As the tuning fork maintains an oscillation of constant frequency, ordinary pressure changes do not affect the resonance length of the gas; but as its velocity varies with temperature, correction therefor must be made.

From the accompanying curve (Fig. 2) it may be noted that the resonance amplitude is very perceptibly reduced by a slight variation in the length of column, as indicated by the ammeter.

At the frequency employed in various devices, a change of 0.01 per cent from the resonance length causes the column to be thrown out of resonance from the maximum amplitude indicated by the meter. Thus, a change in the density of the gas sufficient to cause a change in the resonance length of 0.01 per cent is readily indicated; and if the resonance length of one of the gases in the binary mixture is known, its quantitative relation to the other known element can be determined.

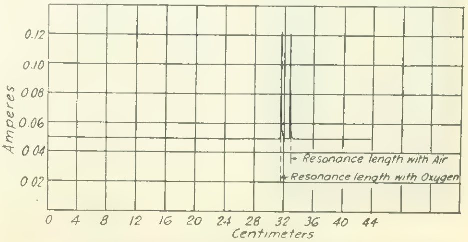

Fig. 2—Relation between Length of Chamber and Ammeter Readings of Tuning Fork Driver Circuit

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[1] Received December 12, 1922.

To operate the device, the chamber length is first adjusted to a point beyond the resonance length of the gas to be tested. The gas is then admitted, and when the previous content has been expelled the circuit is closed and the current actuating the fork is noted, the chamber length being reduced until the point of maximum current amplitude is reached. This point is indicated by changing the chamber length in both directions, a sharp falling off of the current occurring in both cases. The dial and temperature readings are then compared with calibrated figures.

If the gas is continuously passing through the chamber, a minute or so is required for adjustment, readings, and comparisons. Otherwise, several minutes may be necessary to expel the previous gas content of the chamber. Correction for any vapor present may be made in connection with that for temperature. An instrument is calibrated at a specific temperature and requires no further calibration. It has no delicate parts and there is little or no wear or deterioration. The current consumption is about 0.15 ampere, thus permitting the use of ordinary dry cells as a source of energy. The tuning fork is operated at any voltage between 4 and 12, but a potential of 6 volts is preferable.

A specific application of this device is in the determination of the hydrogen content in electrolytic oxygen. Owing to the large density differences between these two elements, a small percentage of hydrogen causes a very perceptible change in the resonance length of the gas column. The difference between the resonance length of a pure oxygen column and of that gas with hydrogen added may be calculated by the equation below, in which L represents the resonance length of oxygen,

$$L = \frac{V}{f}$$

If f, the frequency, equals 1000 cycles, and V at ° C. is 317.2 mm. per second,

$$L = 31.72 \text{ cm.}$$

The resonance length of hydrogen at the same frequency and temperature is 126.95 cm.

From the resonance amplitude curve it may be noted that a change of 0.01 per cent in the resonance length gives a comparatively large indication; and as the resonance length varies as the square root of the gas density, a change of 0.1 per cent by volume of hydrogen in oxygen causes a notable change in the resonance length of the column. Therefore, under proper conditions and with correction factors included, it is possible to indicate the presence of hydrogen by a fractional part of 0.1 per cent.

The same applies to other gas mixtures, as, for example, air and sulfur dioxide, in which case less than 1 per cent of SO_2 is readily indicated.

When three gases are present, two bearing a fixed relationship to each other, by determining the purity of one element the percentages of the other two may quickly be ascertained.

The cylinders can be electrically maintained at constant temperature by means of a resistance wire wound around them and connected with a thermostatic control element. This arrangement eliminates the correction factor for temperature and also permits the adjustment of cylinders at a point from which the meter indicates approach to resonance condition; or the cylinders can be brought to resonance adjustment and any variation from that indication can be noted continuously.

For close determinations within narrow limits the entering gas should be dried, as by discharge through a sulfuric acid wash bottle or suitable means. It can also be saturated at a fixed temperature, in which case a correction factor for water vapor can be introduced.

Arthur Lowenstein Research Fellowship

A gift of $2500 a year, for three years, for the purpose of creating the first research fellowship in connection with the newly organized Institute of Meat Packing at the University of Chicago, has been made by Arthur Lowenstein, vice president of Wilson & Company. This research will be carried on under Prof. E. O. Jordan, head of the Department of Bacteriology of the university. Mr. Lowenstein is one of the special lecturers in the Institute of Meat Packing at the university, as well as chairman of the Committee on Scientific Research of the Institute of American Meat Packers and investigations associated with the packing industry.

ARTHUR LOWENSTEIN

A series of lectures under the joint auspices of the School of Commerce and Administration of the University of Chicago and the institute has been inaugurated, and courses of instructions have been arranged so that employees in the packing plants have a better opportunity to fit themselves for their work. The courses are intended primarily for those occupying minor executive positions and who are ambitious to become executives. Both day courses for full-time study and evening courses are announced.

The packing industry has always been known for its achievements in applied science and prosecution of fundamental research. This work has been done in the individual plants and laboratories, and the establishing of this Arthur Lowenstein Research Fellowship at the university will be watched with great interest and, it is believed, constitutes not only an advance in education, but also an important undertaking in scientific research.

Evening courses for employees of the meat-packing industry are now being conducted at the downtown rooms of the university. Correspondence courses are expected to follow after January 1, 1924, and a four-year curriculum of day courses will probably be inaugurated on October 1, 1924.

Meeting of Advisory Board on Dictionary of Specifications

A meeting was held on October 24, 1923, of the Advisory Board organized to act in an advisory capacity to the Department of Commerce in compiling material for and publishing a handbook of specifications for commodities purchased by federal, state, and municipal governments and public institutions.

At the meeting of the Advisory Board, at which there were present representatives from all but one of the organizations represented on the board, unanimous approval was voted for the proposed plan for issuing in convenient form a thoroughly classified list of all known existing commodity specifications.

The board voted unanimously for the creation by the Secretary of Commerce, as chairman of the board, of three committees from its membership to render reports for the approval of the board on the subjects of (1) classification of commodity specifications, (2) form and size of the publication, and (3) scope of the proposed handbook or encyclopedia of specifications.

Robert Brown and the Discovery of the Brownian Movement[1]

By Lyman C. Newell

Boston University, Boston, Mass.

ROBERT BROWN, the eminent botanist and discoverer of the Brownian movement, was born December 31, 1773, at Montrose, Scotland, the son of an Episcopal clergyman. In 1787 he entered Marischal College, Aberdeen, but two years later went to Edinburgh University, where he studied medicine, and received his degree of M.D. While at Edinburgh he also studied botany, and his interest in botany attracted the attention of John Walker (1731–1803), professor of natural history in the university. He obtained a commission, in 1795, as "ensign and assistant surgeon," in a Scottish regiment, and served in the north of Ireland.

Robert Brown

In 1798 he made the acquaintance of Sir Joseph Banks. Deciding to devote himself to botany, he resigned his army commission in 1800, and in 1801, on the recommendation of Sir Joseph Banks, he was engaged as naturalist of an expedition sent out to explore and survey the coasts of Australia, which at that time were almost unknown. The expedition returned to England in 1805, and Brown brought back nearly four thousand species of Australian plants, many of which were new to science. He was immediately appointed librarian of the Linnean Society. In this position, though not one of great emolument, he had abundant opportunities for research and writing. In 1810 he published the first volume of his great work, the "Prodromus Florae Novae Hollandiae et Insulae Van Dieman," which did much to further the general adoption of de Jussieu's natural system of plant classification. The merits of this book were immediately recognized by scientists, and it gave the author an international reputation among botanists. It is rare in the original edition, the author having suppressed it, because the *Edinburgh Review* severely criticized its Latin. With the exception of a Supplement published in 1830, no more of the "Prodromus" appeared.

In 1810 Brown became also librarian to Sir Joseph Banks. On the death of Sir Joseph in 1820, Brown was given the use of his library and collections for life. In 1827 the library and collections were transferred to the British Museum, with Brown's consent and in accordance with the will of the donor. Brown was appointed keeper of the Botanical Department of the British Museum, and he held this position until his death in 1858. Soon after the death of Sir Joseph Banks, Brown resigned as librarian of the Linnean Society, though from 1849 to 1853 he served as its president. He was elected a Fellow of the Royal Society in 1811, and in 1839 was awarded the Copley medal for his "discoveries on the subject of vegetable impregnation." Oxford conferred the degree of D.C.L. on him in 1832, Edinburgh gave him an L.L.D., and in 1838 he was elected one of the five foreign associates of the Institute of France. He died June 10, 1858, in the house in Soho Square, London, bequeathed to him by Sir Joseph Banks. His works, which embrace not only systematic botany, but also plant anatomy and physiology, are distinguished by their thoroughness and conscientious accuracy, and display powers of both minute detail and broad generalization.

Between 1825 and 1834 his publications (up to 1834) were collected and issued in four divisions by Nees von Esenbeck, in German, under the title of "Vermischte Botanische Schriften" (Leipzig and Nuremberg). In 1866 the Ray Society reprinted, under the editorship of J. J. Bennet, his friend and successor in the keepership of the Botanical Department of the British Museum, his complete writings, the "Prodromus" alone excepted, bearing the title "Miscellaneous Botanical Works" (2 volumes with atlas of plates, 1866–1868).

The portrait of Brown shown herewith is a reproduction of an engraving dated May 24, 1837. The engraving was made by Charles Fox from a painting by H. W. Pickersgill, R.A., which has recently been presented to the Linnean Society by some of Brown's friends.

The Brownian Movement

The continuous movements observed by the microscope among minute particles suspended in a liquid were first noticed by Brown in 1827, and these movements were later called "The Brownian movement" in honor of the discoverer. The discovery was made during a physiological-botanical investigation. The investigation is recounted in two magazine articles published in 1828 and 1829. The first article was published in the *Edinburgh New Philosophical Journal*, Vol. 5, April to September, 1828, pp. 358–371. This article is dated July 30, 1828, and bears the title, "A Brief Account of Microscopical Observations Made in the Months of June, July, and August, 1827, on the Particles Contained in the Pollen of Plants; and on the General Existence of Active Molecules in Organic and Inorganic Bodies." The second article was published in the *Edinburgh Journal of Science*, Vol. 1, April to October, 1829, new series, pp. 314–319. It is dated July 28, 1829, and has the brief title, "Additional Remarks on Active Molecules." The first article is the more important.

In giving an account of Brown's investigation which includes his famous discovery, his own words will be used as far as possible. The word "particles" will be substituted for "molecules," and since we are chemists—not botanists—the botanical parts relating to shape and change of shape of the particles will be excluded in favor of the chemical parts dealing with the movements of particles.

His apparatus was very simple. He possessed a double convex lens and also a pocket microscope with two lenses having a delicate adjustment. Nevertheless, he says:

> The observations have all been made with a simple microscope, and indeed with one and the same lens, the focal length of which is about $^1/_{32}$ of an inch.

In his introduction he states his thesis thus:

> The examination of the unimpregnated vegetable ovulum, an account of which was published early in 1826, led me to attend

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[1] Presented before the Section of History of Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

> more minutely than I had done before to the structure of the pollen, and to inquire into its mode of action.

Like most of us, he did not get a quick start, for he states:

> It was not until late in the autumn of 1826 that I could attend to this subject; and the season was too far advanced to enable me to pursue the investigation. Finding, however, in one of the few plants then examined, the figure of the particles contained in the grains of pollen clearly discernible, and that figure not spherical but oblong, I expected, with some confidence, to meet with plants in other respects more favorable to the inquiry, in which those particles, from peculiarity of form, might be traced through their whole course.

His delay was not long, however, and he continues:

> My inquiry on the point was commenced in June, 1827. The first plant examined was *Clarckia pulchella*, of which the grains of pollen, taken from antherae full grown, but before bursting, were filled with particles or granules of unusually large size, varying from nearly $^1/_{4000}$th to about $^1/_{5000}$th of an inch in length, and of a figure between cylindrical and oblong, perhaps slightly flattened, and having rounded and equal extremities.

His next observation reveals the skilled investigator, and for us is intensely interesting.

> While examining the form of these particles immersed in water, I observed many of them very evidently in motion; their motion consisting not only of a change of place in the fluid, manifested by alteration in their respective positions, but also not unfrequently of a change of form in the particle itself. * * * These motions were such as to satisfy me, after frequently repeated observation, that they arose neither from currents in the fluid nor from its gradual evaporation, but belonged to the particle itself.

In these simple words Brown stated the discovery that has subsequently taken such an overwhelmingly important place in chemistry.

Realizing the significance of this observation, he continues along the same line:

> In extending my observations to many other plants of the same natural family, similar motions of particles were ascertained to exist. I found also in their grains of pollen taken from certain plants immediately after bursting an increase in the number of particles.
>
> This great increase in the number of the particles before the grain of pollen could possibly have come in contact with the stigma was a perplexing circumstance in this stage of the inquiry, and I accordingly examined numerous species of many of the more important and remarkable families of the two great primary divisions of phaenogamous plants.
>
> In a great proportion of these plants I remarked the increase of the number of particles after the bursting of the antherae; the particles, of apparently uniform size and form, being then always present; and in some cases, indeed, no other particles were observed, either in this or in any early stage of the secreting organ.
>
> In many plants belonging to several different families the membrane of the grain of pollen is so transparent that the motion of the larger particles within the entire grain was distinctly visible; and it was manifest also at the more transparent angles, and in some cases even in the body of the grain.

The successful outcome with living plants led him to broaden the field. He goes on to say:

> Having found motion in the particles of the pollen of all the living plants which I had examined, I was led next to inquire whether this property continued after the death of the plant, and for what length of time it was retained.
>
> In plants, either dried or immersed in spirit for a few days only, the particles of pollen of both kinds were found in motion equally evident with that observed in the living plant; specimens of several plants some of which had been dried and preserved in an herbarium for upwards of twenty years, and others not less than a century, still exhibited the smaller particles in considerable numbers, and in evident motion, along with a few of the larger particles, whose motions were much less manifest, and in some cases not observable.

He next extends his field still further:

> In this stage of the investigation, having found, as I believed, a peculiar character in the motions of the particles of pollen in water, it occurred to me to appeal to this peculiarity as a test in certain families of Cryptogamous plants, namely, Mosses, and the genus Equisetum, in which the existence of sexual organs had not been universally admitted.
>
> In the supposed stamina of both these families, Mosses and Equiseta, I found minute spherical particles having equally vivid motion on immersion in water; and this motion was still observable in specimens both of Mosses and of Equiseta, which had been dried upwards of one hundred years.

This time he was astonished, but continues:

> The very unexpected fact of seeming vitality retained by these minute particles so long after the death of the plant, would not perhaps have materially lessened my confidence in the supposed peculiarity. But I at the same time observed that on bruising the ovula or seeds of Equiseta, which at first happened accidentally, I so greatly increased the number of moving particles, that the source of the added quantity could not be doubted. I found also, that on bruising the first floral leaves of Mosses, and then all other parts of those plants, I readily obtained similar particles, not in equal quantity indeed, but equally in motion.

Many investigators would have stopped at this point. Not so Brown—he was seeking the whole truth. Like other famous discoverers he reflected, and then acted.

> Reflecting on all the facts with which I had now become acquainted, I expected to find these particles in all organic bodies; and, accordingly, on examining the various animal and vegetable tissues, whether living or dead, they [the particles] were always found to exist; and merely by bruising these substances in water, I never failed to disengage the particles in sufficient numbers to ascertain their apparent identity, in size, form, and motion, with the smaller particles of the grains of pollen.
>
> I examined also various products of organic bodies, particularly the gum resins, and substances of vegetable origin, extending my inquiry even to pit-coal; and in all these bodies particles were found in abundance. I remark here, also, partly as a caution to those who may hereafter engage in the same inquiry that the dust or soot deposited on all bodies in such quantity, especially in London, is entirely composed of these particles.
>
> One of the substances examined was a specimen of fossil wood, found in Wiltshire oolite, in a state to burn with flame; and as I found these particles abundantly, and in motion in this specimen, I supposed that their existence, though in smaller quantity, might be ascertained in mineralized vegetable remains. With this in view a minute portion of silicified wood, which exhibited the structure of Coniferae, was bruised, and particles in all respects like those so frequently mentioned, were readily obtained from it. Hence I inferred that these particles were not limited to organic bodies nor even to their products.

The discovery of moving particles in substances on the borderline between organic and inorganic matter led him to test the hypothesis just made. So he says:

> To establish the correctness of the inference, and to ascertain to what extent the particles existed in mineral bodies, became the next object of inquiry. The first substance examined was a minute fragment of window glass, from which, when merely bruised, I readily and copiously obtained particles agreeing in size, form, and motion with those which I had already seen.
>
> I then proceeded to examine, and with similar results, such minerals as I either had at hand or could readily obtain, including several of the simple earths and metals, with many of their combinations.
>
> Rocks of all ages, including those in which organic remains have never been found, yielded the particles in abundance. Their existence was ascertained in each of the constituent minerals of granite; a fragment of the Sphinx being one of the specimens examined.

Convinced of the truth of his discovery, he says:

> To mention all the mineral substances in which I have found these particles, would be tedious; and I shall confine myself in this summary to an enumeration of a few of the most remarkable. These were both of aqueous and igneous origin, as travertine, stalactites, lava, obsidian, pumice, volcanic ashes, and meteorites from various localities. (I have since found the particles in the sandtubes, formed by lightning, from Drig in Cumberland.) Of metals I may mention manganese, nickel, plumbago, bismuth, antimony, and arsenic. In a word, in every mineral which I could reduce to a powder sufficiently fine to be temporarily suspended in water, I found these particles more or less copiously.

The second article adds little of fundamental value to the discovery described in the first article. However, a few portions of the second article are significant.

> About twelve months ago I printed an account of Microscopical Observations made in the summer of 1827, on the Particles contained in the Pollen of Plants; and on the general Existence of active Molecules in Organic and Inorganic Bodies.
>
> I have remarked that certain substances, namely, sulfur, resin, and wax, did not yield active particles, which, however, proceeded merely from defective manipulation; for I have since readily obtained them from all these bodies; at the same time I ought to notice that their existence in sulfur was previously mentioned to me by my friend, Mr. Lister.

He adds this information about his lenses:

> In prosecuting the inquiry subsequent to the publication of my Observations, I have chiefly employed the simple microscope mentioned in the Pamphlet, as having been made for me by Mr. Dollond, and of which the three lenses that I have generally used, are of a 40th, 60th, and 70th of an inch focus.
>
> Many of the observations have been repeated and confirmed with other simple microscopes having lenses of similar powers, and also with the best achromatic compound microscopes, either in my own possession or belonging to my friends.

His summary is quoted in full:

> The results of the inquiry at present essentially agree with that which may be collected from my printed account, and may here be briefly stated in the following terms, namely:
>
> That extremely minute particles of solid matter, whether obtained from organic or inorganic substances, when suspended in pure water, or in some other aqueous fluids, exhibit motions for which I am unable to account, and which from their irregularity and seeming independence resemble in a remarkable degree the less rapid motions of some of the simplest animalcules of infusions. That the smallest moving particles observed, and which I have termed Active Molecules, appear to be spherical, or nearly so, and to be between $^1/_{20,000}$th and $^1/_{30,000}$th of an inch in diameter; and that other particles of considerably greater and various size, and either of similar or of very different figure, also present analogous motions in like circumstances.
>
> I have formerly stated my belief that these motions of the particles neither arose from currents in the fluid containing them, nor depended on that [internal] motion which may be supposed to accompany its evaporation.

In Jean Perrin's little book entitled "The Brownian Movement and Molecular Reality," the famous French chemist says:

> They [the particles] go and come, stop, start again, mount, descend, remount again, without the least tending toward immobility. This is the Brownian movement, so named in memory of the naturalist Brown who discovered it in 1827 (very shortly after the discovery of the achromatic objective), then proved that the movement was not due to living *animalculae*, and recognized that the particles in suspension are agitated the more briskly the smaller they are.

If we believe with Perrin and others in the reality of molecules and their continuous movements, then the name of Robert Brown will be immortal.

The Testing of Chemicals in the Bureau of Chemistry from 1920 to 1923[1]

By G. C. Spencer

Bureau of Chemistry, Washington, D. C.

The practice of testing all chemicals purchased at the Bureau of Chemistry has been systematically followed for over twenty years, with results that have demonstrated the sound economy of this policy. As an illustration of the necessity for watchfulness on the part of Government purchasing officers, instances have been noted where chemicals that had been rejected by the Bureau of Chemistry were hauled away by the dealer and delivered directly to one of the neighboring bureaus, which accepted these supplies without examination.

It is the purpose of this paper to discuss some of the cases that have arisen in the bureau during the past three years with a view to showing:

1—The nature of the objections that may be raised by the purchasers.
2—In what respects the manufacturers may be to blame.
3—A few suggestions that might possibly lead to better understandings between dealers and customers.

The following examples of chemicals rejected by the bureau will help to illustrate in some measure the buyer's point of view:

Calcium oxide, discolored by iron and contained about 36 per cent of magnesium oxide
Hydrochloric acid, 40 parts per million of arsenic. A replacement order contained 5 parts per million
Fuming sulfuric acid, 50 per cent; not over 25 per cent free SO_3 found, and was liquid at room temperature
Lead carbonate, 5.37 per cent water-soluble matter
Absolute methanol, 5.5 mg. residue per 100 cc.
Sodium hydroxide, high in sulfates and chlorides
Sulfuric acid, 10 parts per million of arsenic
Ammonium thiocyanate, iron enough to give it a pink color
Calcium chloride, 8.9 per cent alkalinity as CaO
Potassium carbonate, 8 per cent foreign matter. The second and third replacement orders showed no improvement
Absolute ether from two different dealers; both reacted strongly with sodium and contained aldehydes
Benzene, put up in wet bottles
Acetic acid 99.9 per cent; only 99.6 per cent was found. The manufacturer had depended upon the titration method of assay while the bureau used the cryoscopic method. As soon as the manufacturer adopted the latter method, he had no further trouble in supplying the desired acid strength
Chlorinated lime; two samples contained not over 22 per cent available chlorine
Ethyl acetate, 16 mg. residue from 100 cc.; brown color with sulfuric acid
Carbon disulfide, 6 mg. residue from 100 cc.
Amyl acetate, packed in dusty bottles as seen by suspended matter. Two replacement orders were rejected before a satisfactory lot was received. The last of these had a residue of 8 8 mg. from 100 cc.
Magnesium oxide, iron and sulfates present

Here also may be included the chemical samples that are just on the line of acceptability, not quite bad enough to send back but applicable only for certain kinds of work. Such samples cause more annoyance and take more time than any others. For example, the specifications of the General Supply Committee require a hydrochloric acid strength of 36 per cent and a sulfuric acid strength of 95 per cent. It has happened a number of times that the acid strengths found would run from 2 to 4 per cent below the required amounts. On at least one occasion the dealer in question offered to adjust the price to conform to the lower strength found.

Summarizing the objectionable features in the list just enumerated, it is found that the manufacturers are at fault in permitting dirty or wet bottles to be used for purified chemicals. This statement is justified by the number of cases, already cited in this paper, of distilled organic liquids which should be free from weighable residue, at least, if they had been handled carefully in preparation. The mistakes of the manufacturers lie in their packing and shipping departments fully as much as in their preparation rooms. This point has been emphasized in letters to chemical manufacturers, and usually their replies have indicated a good spirit of coöperation and a promise to see that carelessness would be eliminated as far as possible. On the other hand, the customer shares some of the blame. Instead of reporting grievances in a friendly spirit, he often complains to his associates of the poor quality of goods manufactured by the firm in question, does much to give the company a bad name, and buys from some one else.

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[1] Presented before the Division of Industrial and Engineering Chemistry at the 66th Meeting of the American Chemical Society, Milwaukee, Wis., September 10 to 14, 1923.

Wherever possible all chemicals purchased should be examined to ascertain their fitness for the purpose for which they are intended. This does not always mean an elaborate chemical analysis. A careful inspection is often sufficient to detect particles of dirt, foreign-colored bodies, and moisture, while in cases of volatile substances the lack of residue at once proves the absence of heavy metals and of many minerals.

Since May 1, 1920, the total number of chemicals passed upon in the Bureau of Chemistry is 465, from 40 different dealers. Of these chemicals 32 (6.9 per cent) have been returned as unfit for the bureau work. Reference may here be made to a previous article on this same subject.[2] During the period from 1911 to 1915, mentioned in Buc's article, about 1300 samples were examined, of which 50 (3.8 per cent) were found to be unsatisfactory. During the war the percentage was three times as much.

The conclusion to be drawn from these statements is that American manufacturers are, for the most part, making satisfactory chemicals. There is still a great deal to be done, however. The examples cited in this paper, as well as those given by Buc, show an unwarranted carelessness in preparing and shipping chemicals. Furthermore, all chemists who are experienced in examining those chemicals which bear analyses on their labels know very well how little dependence can be placed on such statements.

In 1921 the writer sent 119 copies of a circular letter to members of the Association of Official Agricultural Chemists, asking for specific statements of unsatisfactory reagent chemicals. Only 17 replies were received, and of these only 5 had any complaints to make. From the lack of response to this letter it may be assumed that the quality of reagents purchasable in this country is satisfactory; on the other hand, it may be assumed that most of the recipients of this letter were satisfied to take the legend C. P., or the label analysis, on faith, and to trust to luck.

If analytical chemistry is to be defined as the art of taking pains, the necessity for a careful selection of reagents at the time of purchase cannot be overstated.

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[2] Buc, This Journal, **11**, 1140 (1919).

Personals

Irving E. Adams, chemical engineer and glass consultant, has terminated his contract with the J. E. Marsden Glass Works, Inc., Ambler, Pa., and is continuing his general glass consulting work at 623 North Spring Garden St., Ambler, Pa.

Fred W. Ashton, of the Structural Materials Research Laboratory of the Portland Cement Association, has been detailed to the Bureau of Standards.

R. C. Atwater, formerly employed as chemical engineer with the Beech-Nut Packing Co., is now engaged as chemical engineer with the Atlantic Refining Co., Philadelphia, Pa.

John J. Boyle has resigned his position with G. S. Alexander & Co., Inc., and has entered the brokerage field in chemicals and fertilizer materials, with offices at 140 Liberty St., New York, N. Y.

Ralph F. Brenner, formerly chief chemist of the H. C. Fry Glass Co., Rochester, Pa., is now connected with the Vitrolite Co., Parkersburg, W. Va.

A. C. Bright has resigned his position as assistant physicist at the Fixed Nitrogen Laboratory, Department of Agriculture, to accept an appointment as experimental engineer in the engineering department of E. I. du Pont de Nemours & Company.

Edward Epstein, chemist at the du Pont Fibre Silk Company's plant at Buffalo, N. Y., was seriously injured on November 2, while at work in the laboratory, when a retort of chemicals flared up, badly burning his face.

Carl Fellers, formerly associated with the Bureau of Chemistry and with the National Canners Association, has been appointed associate professor of the newly established department of food preservation, University of Washington.

Arthur C. Gerlach, formerly of the Bureau of Yards and Docks, Navy Department, has been appointed as an assistant dust explosion prevention engineer and assigned to the office of Development Work of the Bureau of Chemistry, Washington, D. C.

Bernhard G. Hartmann has been transferred from the Chicago Food and Drug Inspection Station of the Bureau of Chemistry to the Food Control Laboratory, Bureau of Chemistry, Washington, D. C.

Lucille Johnson, who recently completed some research under the direction of A. W. Thomas at Columbia University, has accepted a position as instructor in the Household Science Department of the University of California.

Roland M. Kohr, formerly with the National Refining Co., Findlay, Ohio, is now metallurgist and special chemist for the Grasselli Chemical Co., Clarksburg, W. Va.

Norman W. Krase has resigned his position in the Fixed Nitrogen Research Laboratory, to accept an instructorship in the Department of Chemical Engineering at Yale University.

M. A. Lamme, formerly engaged in chemical and geological work in South America, has recently joined the research staff of the manufacturing organization of the Western Electric Co., Hawthorne Works, Chicago, Ill.

Arthur D. Little, president of Arthur D. Little, Inc., was elected life member of the Corporation of the Massachusetts Institute of Technology at the fall meeting of the corporation held on October 24, 1923.

Benno Lowy, of San Francisco, Calif., a chemist associated with the Pacific Chemical Laboratories, has been reappointed official chemist of the New York Produce Exchange for the Pacific Coast territory and the Orient.

L. P. Miller has left the employ of the National Aniline & Chemical Co., Buffalo, N. Y., to accept an appointment in the control laboratory of the mill of the West Virginia Pulp & Paper Co., Piedmont, W. Va.

B. H. Nissen, who received his B.S. from the University of Wisconsin in June, 1923, has accepted an appointment as research chemist for the Blue Valley Creamery Co., Chicago, Ill.

B. Sandmann, who recently spent some time in Venezuela, has returned to New Orleans and will continue his former business as consulting engineer, specializing in animal and vegetable carbons.

Earl A. Sewell, who received his degree of chemical engineer from the Tri-State College of Engineering, Angola, Ind., in August, 1923, has accepted a position as chemist in the laboratory of the Huron Portland Cement Co., Alpena, Mich.

Philip P. Sharples, who for the past eighteen years has been in the employ of The Barrett Co., is now connected with the Palos Verdes Project, Redondo Beach, Calif.

Harold Stose, who was connected with the Research Laboratory of Applied Chemistry at the Massachusetts Institute of Technology, has accepted an appointment in the chemical department of the Hood Rubber Co., Watertown, Mass.

Victor H. Transue resigned from his position in the laboratory of the Barber Asphalt Co., Maurer, N. J., to accept a position in the research laboratory of the Barrett Co., Frankford, Pa.

J. E. Underwood has resigned his position as research chemist with the Radium Emanation Corporation, to join the staff of the National Lime Association as assistant chemical director.

A. T. Ward, who has been associated with the Union Carbide & Carbon Corp., New York, has gone in business for himself, operating under the name of Acme Coal Mining Sales Corp., 20 Broad St., New York, N. Y.

AMERICAN CONTEMPORARIES

John Maxson Stillman

JOHN MAXSON STILLMAN was the first executive head of the Chemistry Department of Leland Stanford Junior University. Here he found an atmosphere so congenial, a field of work so full of possibilities, and a burden of responsibilities so great that it would have been difficult for him to have migrated elsewhere, even had he so desired. At any rate, here he has stayed, and here he has labored and rested and labored again, until today finds him an emeritus of six years' standing, still laboring and resting and laboring again.

To the casual acquaintance of the street, the club, the social circle, he is always the embodiment of gentlemanly grace and affability; genuinely cultured and quick of wit; the ideal toastmaster who can preside with a light and airy dignity and never say "that reminds me of a story," and who can keep the revelers in merriment without recourse to the slightest suggestion of coarseness. Socially he is an artist of high rank.

John Maxson Stillman

His services to Stanford University have been of fundamental importance. As the guiding hand in the upbuilding of the chemistry department, his work was so well done that, since his retirement, little has been necessary except to follow along the lines of general policy which were established under his régime. Within the department he maintained himself in the fortunate position of one possessed of almost absolute power, but wise enough to wield it as little as possible. His willingness to listen most patiently to opponents, and to discuss with perfect calmness and fairness all the intricacies of a difficult situation, together with his firm insistence on the right of the junior members of the staff to teach as they thought best, were always potent factors in keeping the waters smooth. Yet every one knew that the power was there and that if the occasion should arise the sword would be drawn.

In the broader field of general university administration Stillman has also done yeoman's work. He has served for considerable and often very delicate and difficult periods as vice president and as close councilor to both president and trustees. Here his administrative talent showed itself in a way quite other than that of the head professor of chemistry. No longer dictator, he became the loyal and zealous agent of his superiors in power. He accorded to those in authority over him that same respect and allegiance which he expected and knew so well how to win from those under him. But by no means did he ever become the mere henchman. In council he would present his views with all the force he could muster, and he often won his point through better information as to the details of a situation, together with an unusually keen ability to visualize and express clearly the possible and probable results of a mooted policy. But the decision once taken, whether for or against him, became in his eyes inviolable law, and if, in the course of the years, there have been any who have conceived for him anything akin to dislike or enmity, it is fairly safe to attribute it to their having crashed against his stone-wall defense of the authority of his superiors.

As a teacher, Stillman was always a clear and convincing lecturer, and he courted intimate discussions with his pupils. That these, almost without exception, came to admire and revere him, is shown clearly enough by the ease with which a substantial sum was raised among them to establish the Stillman Fellowship Fund as a testimonial at the time of his retirement.

As an investigator he has numerous titles to his credit, but, the burdens of administration coming on him so comparatively early in life, he was forced pretty nearly to renounce research "in order to make it possible for others to do the work." However, the creative chemist in him had to survive somehow, and he turned his attention to the historical aspects of his science, and numerous essays in this field have appeared from his pen. Since retirement his activities in this direction have increased, and a "Life of Paracelsus" has already appeared, and "The Story of Early Chemistry," conceived on unique lines, is in the hands of the printer.

And so an unusually sensitive nature, buoyed up by a high regard for spiritual values, has traveled through the vicissitudes of life to the golden harvest time. It has already been a long and useful life, and, happily, time still goes on.

S. W. Young

Calendar of Meetings

American Institute of Chemical Engineers—Winter Meeting, Washington, D. C., December 5 to 8, 1923.

American Petroleum Institute—4th Annual Meeting, St. Louis, Mo., December 11 to 13, 1923.

American Association for the Advancement of Science—75th Meeting, Cincinnati, Ohio, December 27, 1923, to January 2, 1924.

Federated American Engineering Societies—Annual Meeting, Washington, D. C., January 10 and 11, 1924.

Franklin Institute—Annual Meeting, Philadelphia, Pa., January 16, 1924.

American Society of Heating and Ventilating Engineers—Annual Meeting, New York, N. Y., January 22 to 25, 1924.

American Ceramic Society—Atlantic City, N. J., February 4 to 9, 1924.

American Chemical Society—67th Meeting, Washington, D. C., April 21 to 25, 1924.

American Electrochemical Society—Spring Meeting, Philadelphia, Pa., April 24 to 26, 1924.

NOTES AND CORRESPONDENCE

A Device for Water Analysis and Slow Filtration

Editor of Industrial and Engineering Chemistry:

In THIS JOURNAL, **15,** 901 (1923), Andrew C. Simmons describes a labor-saving filtration device. The writer used such devices for many years and can testify as to their great practical convenience and economy of time. No chemist should be content to "park" in front of a filter and slowly dribble a poorly filtering solution through it by hand. But we think that Mr. Simmons' explanation of the operation of his device is mistaken. It is chiefly a surface tension phenomenon. The bubble of air imprisoned in *D* (see his figure), approximately spherical in shape, is gradually drawn into the main delivery tube as the level of the evaporating liquid lowers, and in the process it becomes distorted and drawn out until flotation overcomes surface tension causing a portion of the bubble to break off and rise into the flask. This rupturing of the surface film is the whole thing, and the necessary difference in pressure at *D* and *E* is the pressure required to distort the bubble and increase its surface. It might be observed in passing that surface tension phenomena play a far greater part in hydrostatics than many laboratory workers realize.

An equally effective filtration device can more easily be made without the appendage *AD*. A small hole at *A*, flush with the surface of the main tube and about 10 mm. above the tip, is sufficient. Upon the size of the hole will depend the height of the water column *AE*, at which it vents. (Surface tension again.) A convenient diameter is 3 to 4 mm. The smaller the hole the greater will be the fluctuation of level. In putting such a device into operation, after filling and assembling, a bit of wet filter paper is placed over the hole at *A*. With care, the whole can then be inverted over the filter or evaporating dish without spilling. When adjusted the paper seal is removed.

With all these pneumatic devices it should be remembered that heating of the air above the solution in the flask introduces a disturbing element.

CHARLES VAN BRUNT

GENERAL ELECTRIC COMPANY
SCHENECTADY, N. Y.
September 14, 1923

. . . .

Editor of Industrial and Engineering Chemistry:

The letter from Mr. Van Brunt with his suggested explanation of the mechanism of the automatically regulated flow of liquid in the device which I described has interested me a great deal. At the time that I made this device I was a student at the University of Florida. It seemed to me that much time was wasted in laboratory filtration and evaporation processes which could be easily saved by the use of an automatic feed. After several trials, I finally hit upon the present scheme which seemed to solve the problem satisfactorily.

Since that time I have realized that the explanation which I gave was not adequate. Mr. Van Brunt is certainly right in his contention that surface tension plays a role in the process. As I conceive the process, it occurs as follows:

We have an inverted flask, partially filled with liquid and attached by means of a stopper in the neck to a long, vertical glass tube which dips into the liquid in an evaporating dish below. Some of the liquid from the flask empties down the tube, but finally the flow ceases, and will not begin again until more air is allowed to enter the space in the flask above the liquid. The air in this space is in a "stretched" condition, so to speak—that is, its pressure is less than that of the atmosphere, and the difference between the two is just equal to the hydrostatic pressure of the column of liquid extending from the surface of the liquid in the flask to the surface of the liquid in the dish below. In this column at the level of the liquid surface in the dish the pressure is atmospheric, but it rapidly decreases with the height of the column. If we are working with water as the liquid, the pressure falls off about eight hundred times more rapidly in ascending inside the tube than it does outside in the air, because of the difference in density of water and air. If we had either a small hole in the glass tube (described by Mr. Van Brunt), or a small open arm attached to the tube (as in my case) at a distance of, say, a few centimeters above the liquid in the dish, the pressure in the water at the level of the opening would be considerably less than that of the atmosphere at the same point, and we would expect air to force its way, as bubbles, into the water column. And so it would, were it not for the surface tension of the bubble film. The combined effect of the pressure in the water and of the surface tension prevents the growth of the incipient bubble and hence prevents the entrance of the air. However, as the water level in the dish falls—say, by evaporation—the effect is exactly the same as though the tube were pulled up out of the water a small distance; the height of the opening above the liquid is increased, and this means that the pressure in the water at the level of the opening is now much less than before and that the air bubbles can now form and rise into the flask. A large flow of water from the flask follows, and as the level in the dish rises again the original conditions are restored.

ANDREW C. SIMMONS

OHIO STATE UNIVERSITY
COLUMBUS, OHIO
November 1, 1923

Adsorption of Dyes by Gelatin

Editor of Industrial and Engineering Chemistry:

In reference to the work of Briggs and Bull and also of Reinmuth and Gordon, on "Effect of Hydrogen-Ion Concentration on Adsorption of Dyes by Wool and Mordants" [THIS JOURNAL, **15,** 818 (1923)], I have found similar results in the adsorption of dyes by gelatin.

HALSEY E. SILLIMAN

NEW YORK, N. Y.
October 30, 1923

Metric System—Correction

On page 996 of the October, 1923, issue of THIS JOURNAL we gave the essence of the motion on the metric system as originally presented by the Committee on the Metric System at the Council meeting in Milwaukee. This motion, however, was returned to the committee for amendment and the motion as finally adopted reads:

> **All articles relating to laboratory test of procedure published in any of the journals of the AMERICAN CHEMICAL SOCIETY shall contain dimensions expressed metrically. Other equivalents may be added where the author so desires.** [See page 113, Proceedings, *J. Am. Chem. Soc.*, **45** (1923).]

Advertising Abuses

Editor of Industrial and Engineering Chemistry:

The News Edition of October 20, 1923, contained an editorial on "Advertising the Chemist," which pointed out some of the evils arising from the use of the chemist in connection with advertisements, especially those that exploit some device, material, or substance of supposedly unusual merit.

Both science and the chemist are exploited frequently by such means. The public seems to swallow the bait, hook and sinker, if science is appealed to in the advertisement. Too great a protest in our professional journals can hardly be made against such abuses. Generally, the advertising agency is to blame in so distorting facts. But it may well be asked if the chemist is not sometimes to be blamed for allowing such procedures to go free by failing to make a protest or, what is worse, by permitting himself to be used in a field in which he is not expert.

Our pure food and drug laws aim to protect the public from adulterated and misbranded materials. Certain abuses are prohibited by these laws and false claims concerning the healing or curative effects of products cannot now be made. These laws do not touch cosmetics and they do not apply to statements concerning the nutritive value of foods. The American Medical Association enjoys pointing out the absurdities dealt in by producers of the cosmetics, but no one seems to be interested in false nutritional claims on package goods and in advertisements.

In connection with this kind of misinformation and exploitation of science and the chemist, there are two types of abuse—absurd claims concerning the merits of the food being advertised, and false and misleading statements concerning some competing food or a food which the advertiser seems to think is unnecessary or harmful. For example, a certain health food company advertises on its package foods that the food contained therein has none of certain normal ingredients of another food, which ingredients are labeled poisons by the health food company. The food so attacked is a staple food in great demand and is perfectly wholesome.

The Federal Trade Commission is sometimes interested in such matters. Advertising clubs are beginning to be interested and sometimes act quite effectively in ending an abuse. The chemist through his professional organizations and journals should be interested and should take a firm and ethical stand on such questions.

C. ROBERT MOULTON

INSTITUTE OF AMERICAN MEAT PACKERS
CHICAGO, ILL.
November 16, 1923

A. O. A. C. Meeting

The Association of Official Agricultural Chemists held its annual meeting at the Raleigh Hotel, Washington, D. C., November 19 to 21, 1923. C. A. Browne, the newly appointed chief of the Bureau of Chemistry, delivered a few words of greeting in behalf of his organization. He warned the association against branching off into research work, stating that its chief function and value lie in the development and elaboration of accurate analytical methods. A man must be a good analyst before he can be a research chemist. This ideal the association has always maintained and he urged the members not to change their course.

Harvey W. Wiley, honorary president, addressed the general meeting on Tuesday morning. This was the best attended session of the entire convention. Dr. Wiley's extemporaneous talk is always looked forward to as the bright spot of the convention and he did not disappoint his hearers. Departing from the subject of strictly agricultural chemistry, he stressed the importance of preparedness in time of peace and briefly but forcibly outlined the history of chemical warfare, referring to it as a new epoch in the history of chemistry. He believes that the maintenance of our Chemical Warfare Service is of immense practical importance to any future wars that may arise and that chemical warfare has now been developed into a distinct arm of our defense service; that the dye industry has also been established in this country on a basis so solid that it will resist all the economic warfare waged against it by misinstructed but perhaps patriotic citizens. In closing, Dr. Wiley urged the members to do all in their power properly to develop this industry so that our Chemical Warfare Service will be in a position to command at once, if necessary, all the poisonous gases which it needs in the defense of our country.

The association endorsed the Prize Essay Contest of the AMERICAN CHEMICAL SOCIETY in the following resolution:

Resolved, That this Association wishes to go on record as heartily endorsing the campaign inaugurated by the American Chemical Society to educate the American people to a better understanding of chemistry, its possibilities, and its applications to everyday life.

The officers for the coming year are: Honorary President, H. W. Wiley; President, R. E. Doolittle; Vice President, C. A. Browne; Secretary-Treasurer, W. W. Skinner; additional members of the Executive Committee, E. M. Bailey and P. B. Dunbar.

Changes in U. S. Pharmacopoeia Tenth

We give below lists of proposed "admissions" and "deletions" for the U. S. Pharmacopoeia Tenth. The first list contains additional titles that have been proposed. The second list consists of other titles, official in the U. S. Pharmacopoeia Ninth, but not recommended for inclusion in the new Pharmacopoeia. In the list of admissions there are a few titles marked with footnote which were reported as "deletions" in earlier lists, but which have been admitted through the action of the Referee Committee on Scope, after careful consideration of the comments received from those who objected to their deletion.

FURTHER ADMISSIONS TO THE U. S. P. X.

Acetum Scillae
Althaea
*Ammonii Salicylas
*Bismuthi Subsalicylas
*Caffeina Citrata
*Calcii Glycerophosphas
Carbon Tetrachloride
Ceratum
Ceratum Cantharidis
*Cimicifuga
*Diacetylmorphinae Hydrochloridum
Emplastrum Belladonnae
Emplastrum Cantharidis
*Extractum Cimicifugae
*Extractum Malti
Fluidextractum Belladonnae Foliorum (new—not in U. S. P. IX; the Fluidextract of the root is also official)
*Fluidextractum Sarsaparillae
Fluidextractum Scillae
Fluidextractum Uvae Ursi
Ipomoea Orizabensis (to replace Scammony)
Liquor Zinci Chloridi
*Maltum
Massa Ferri Carbonatis
Pilulae Phosphori
Quinidinae Sulphas
Quinine Ethylcarbonate ("Euquinine")
*Sarsaparilla
Spiritus Aetheris Nitrosi
*Syrupus Sarsaparillae Compositus
Terebenum
Tinctura Cantharidis
Tinctura Lobeliae
Tinctura Tolutana
Tinctura Valerianae Ammoniata
Tinctura Zingiberis
Unguentum Hydrargyri Nitratis

The following general articles will be included:

Aquae
Aquae Aromaticae
Decocta
Extracta
Fluidextracta
Infusa
Suppositoria
Tincturae
Triturationes

*These titles were announced as deletions but have since been admitted.

DELETIONS

The following additional titles, official in the U. S. P. IX, have not been admitted to the Tenth Revision.

Acidum Oleicum
Collodium Cantharidatum
Extractum Aconiti
Extractum Gentianae
Extractum Opii
Fluidextractum Aconiti
Fluidextractum Gentianae
Fluidextractum Lobeliae
Fluidextractum Nucis Vomicae
Fluidextractum Veratri Viridis
Linimentum Terebinthinae
Liquor Sodii Glycerophosphatis
Oleatum Hydrargyri
Oleoresina Cubebae
Oleum Sesami
Opium Deodoratum
Pilulae Ferri Iodidi
Pilulae Rhei Compositus
Pulvis Aromaticus
Scammoniae Radix (replaced by Ipomoea Orizabensis)
Serum Antidiphthericum Siccum
Serum Antitetanicum Siccum
Spiritus Juniperi Compositus
Tinctura Cannabis
Tinctura Cinnamomi
Trochisci Cubebae
Trochisci Potassii Chloratis

Expressions of opinion regarding these proposed changes are desired, and should be submitted to the general chairman, E. Fullerton Cook, 636 S. Franklin Sq., Philadelphia, Pa.

WASHINGTON NOTES

Internal Revenue Regulations

Work is progressing satisfactorily on the revision of Internal Revenue Regulations 60, "Relative to Intoxicating Liquor," and it is hoped that they can be put into effect within a few weeks. These regulations have received the attention of the Alcohol Trades Advisory Committee, upon which the American Chemical Society has a representative, and were first submitted to this committee in July.

Tariff Commission Activities

The work of the Tariff Commission, so far as we are interested, centered during the past month in the various hearings that were held. On November 5, applications were heard for an increase and also for a decrease in the present duty on oxalic acid. The Victor Chemical Company, of Chicago, applied for an increase of 50 per cent in the 4 cents per pound duty on this chemical, whereas representatives of R. W. Greff & Company, of New York, asked for a decrease. Both sides waived rights to submit briefs and final arguments and the case was closed so far as evidence was concerned. The next step is for the Commission to report its findings to the President.

On November 7, 1923, the barbital hearing was held. A. S. Burdick, president, and E. H. Ravenscroft, vice president of the Abbott Laboratories, Chicago, Ill., appeared in defense of the application for an increase of 50 per cent in the present rate of duty of 25 per cent. No one appeared in opposition and the case was closed. Statistics were given showing that before the war this product was imported at $7 and sold for $21 per pound and that now the domestic product sells to the drug trade for $8.

The hearing on barium peroxide was held on November 9. The J. H. R. Products Company, of Willoughby, Ohio, the sole manufacturer of this product in the United States for sale in the open market, applied for an increase of at least 2 cents per pound in the present duty of 4 cents per pound. John Bene & Sons, Inc., of Brooklyn, applied for a decrease of at least 1 cent per pound, their chief contention being that if the duty was increased they could not afford to import barium peroxide in future and would be forced to buy from this one domestic manufacturer who, they were afraid, would raise his price. Witnesses were given until November 20 to file final briefs.

The Tariff Commission published the actual costs of production in connection with the logwood extract case which was held and closed on November 12. The American Dyewood Company asked that the duty on this product be increased by applying the American valuation principle to the rate of duty in the new tariff act. The Logwood Manufacturing Corporation appeared in opposition. The chief argument advanced by the American Dyewood Company was that the case should be settled on costs in Haiti rather than average cost for the West Indies since Haiti was the principal competing country. Those arguing for a reduction in duty showed that they sold over 80 per cent of the logwood brought in from Haiti to their principal, the National Silk Dyeing Company, of Paterson, and to a domestic manufacturer. They opposed any increase in duty on the ground that the duty, which the Treasury Department has been assessing on the United States value instead of on the foreign market value, was sufficient.

On November 14 the National Electrolytic Company, of Niagara Falls, N. Y., and the North American Chemical Company, of Bay City, Mich., appeared for an increase in the present duty of 1.5 cents a pound on potassium chlorate. They stated that both domestic plants have been entirely closed since 1922, one closing in May and one in December, and that imported potassium chlorate is being sold in New York at less than the American cost of production. The Diamond Match Company were applicants for a decrease in duty to 1 cent a pound. Mr. Fear, representing the Federal Match Corporation, also appeared for a decrease in duty. November 24 was set as the final date for filing brief by the advocates for a decrease. Applicants for an increase were given until December 1 to file a reply. Those opposing an increase testified that they had an old contract with the German manufacturers at an unusually low price which has some time to run but that they did not expect to be able to renew at the same favorable prices.

The field investigations which the Chemical Division has under way including linseed oil, phenol, cresylic acid, and phenolic resins will be pretty well completed by the end of the month.

Graduation Exercises of Chemical Warfare School

Graduation exercises of the recent class of officers undergoing instruction at the Chemical Warfare School were held November 10, 1923, at Edgewood Arsenal. The course completed was one of the Line and Staff Officers' courses which are given from time to time throughout the year. These courses are intended primarily for officers of branches of the Army other than Chemical Warfare and of the Navy and Marine Corps, and are designed to furnish these officers such technical instruction in chemistry and physics as to give them a general knowledge of the characteristics and uses of chemical agents, with particular reference to protective and defensive measures against chemical warfare.

Brigadier General Amos A. Fries, chief of Chemical Warfare Service, delivered an interesting address to the officers, and upon conclusion of the exercises presented diplomas to the following officers who successfully completed the course:

Majors: John A. Baird, Oscar A. Eastwold, Charles E. T. Lull, and James W. Lyon; Captains: Thomas J. Johnston, Charles S. Moyer, Victor Parks, Jr., and George F. Unmacht; First Lieutenant William W. Wise, Chemical Warfare Service. First Lieutenant Giles F. Ewing, Signal Corps. Major Walton Goodwin, Jr., Cavalry; First Lieutenants Milton A. Hill and Emil Krause, and Second Lieutenant Henry J. Hunt, Jr., Infantry; Lieutenants Charles F. Fielding, Ralph G. Moody, Hubert E. Paddock, Charles M. Rockey, William D. Sample, Julian B. Timberlake, Jr., and Andrew M. Parks; Ensigns Edmund W. Egbert and James C. Reisinger, Navy; Lieutenants Franklin F. Lane, and Edwards M. Riley, Naval Medical Corps; and First Lieutenants Herman R. Anderson and Blythe G. Jones, Marine Corps.

Concannon Returns from Europe

C. C. Concannon, chief of the Chemical Division of the Bureau of Foreign and Domestic Commerce, returned to Washington on November 14 from a kaleidoscopic trip to Europe, where he went to study foreign conditions and their bearing upon the work of his division. Among other places he visited London, Paris, Berlin, Brussels, the Hague, Amsterdam, Frankfurt-on-Main and Bernberg, conferring in each city with the commercial attachés and their assistants in an endeavor to give them a clearer understanding of the work of his division and what it is striving to accomplish. He hopes that by carrying to them in this way a picture of just what the chemical industry in America is doing, they will be better able to meet their own problems and to secure for transmission to the Department in Washington chemical information which is analogous to that printed for the United States and which will meet the demands and needs of the American industry. He conferred with many prominent officials in Europe, among them Sir William Alexander, of London, and spent much time with Chemical Trade Commissioner Breithut. As a result of numerous conferences with Commissioner Breithut, arrangements have been made for the latter to begin at once the preparation of a report on the French coal-tar chemical industry. As soon as this is completed he will proceed to Brussels and secure the necessary data to prepare a similar report on the Belgian industry. He will then go to London, Rome, Warsaw, and Prague, spending sufficient time in each city to secure information for the preparation of reports on the coal-tar chemical industry of their respective countries. These reports will be published promptly and will doubtless take the form of Trade Information Bulletins.

While in Germany, Mr. Concannon visited the potash mines just outside of Bernberg, and was to have visited the Hoechst works, but conditions at the time were not propitious for sightseeing.

Census of Lime Manufacturers

The Bureau of the Census will take a census of lime manufacturers covering the calendar year of 1923. Schedules, prepared after conference with associations and others interested in the various industries, will be mailed during the first week in January, and the members of the National Lime Association and all others engaged in the industry are urged to make their reports promptly. The Bureau of the Census, in turn, stands ready to tabulate the data as rapidly as the schedules are received and to publish the tables within a few days after the receipt of the last report.

REPORT ON TANNING MATERIALS

The chestnut blight has been extending its ravages for years, and since the chestnut tree, which is grown only in the eastern part of the United States, affords the most considerable source of tanning materials in this country, the tanning industry has become aroused to the necessity of eradicating this pest. At the request of the Tanners' Council, the Department of Commerce started an investigation to determine what steps should be taken to insure a reasonable domestic supply of tanning materials in the future. The Tanners' Council appointed an advisory committee composed of the leading experts of the country to coöperate with the department in this work. The report, prepared as a result of these investigations, will probably be ready for distribution about the time THIS JOURNAL issues. This report describes the available domestic resources and gives domestic production statistics, as well as consumption statistics for domestic and foreign tanning materials during the year 1922. The figures were compiled from data secured in response to questionnaires sent out to the industry. Production and consumption statistics have been reduced to bark tonnage so that their relative significance to the tanner and the extract producer may be seen at a glance.

Definite recommendations are made as to the course to be pursued in order to assure an adequate supply of domestic raw materials for the future. The situation is regarded as so serious that coöperation from every branch of the industry is deemed absolutely essential. If the industries do not coöperate and present a united front, it is feared that in the event of another international war a serious degree of paralysis of the tanning industry would follow which would make its impress upon every American citizen.

SALINITY OF SEA WATER

The Bureau of Standards has developed an apparatus and procedure by means of which the salinity of sea water may be determined readily on board ship. This work was undertaken at the request of the Committee on Instruments, Apparatus, and Measurements of the Interdepartmental Board on International Service of Ice Observation, Ice Patrol, and Ocean Derelict Destination, and the apparatus is for use on one of the coast guard cutters when on ice patrol duty.

The proportion of salts in sea water varies with time and location as a result of evaporation from the surface and dilution with fresh water. Increase or decrease of the salt content makes a corresponding change in the electrical conductivity, but the indications are made to show directly the corresponding amount of salts present in the water.

This procedure is much quicker and more convenient than the usual chemical titration method. It is intended to enable the scientific observer on the ice patrol work to determine the salinity of samples of sea water as taken or whenever he may desire, rather than only at the end of the season. Thus the data can be made immediately available in case it should be found that a knowledge of the salinity may help in detecting changes in conditions such as shifts of currents, the approach of ice floes or bergs, or other changes affecting navigation.

November 17, 1923

The Nobel Prize

THE award of the Nobel Prize has come to indicate marked scientific progress in the country so fortunate as to have among its workers those who qualify for this signal honor. In the yearly award of these famous prizes Americans have fared better in science than in literature, and this year two of the prizes have come to this continent.

To Dr. Frederick G. Banting and Dr. J. J. R. McLeod the Nobel Prize in medicine has been awarded for the discovery of insulin of which we have read so much during the past year. Working quietly at the University of Toronto with the assistance of fellow workers with whom the prize has been generously shared, little was known of the work until experimental stages had been practically passed and the hundreds of thousands of diabetic sufferers could be told that at last a promising treatment for their relief had been devised through scientific research.

Harris & Ewing

R. A. MILLIKAN

Dr. Banting had already been signally honored by his Government, which granted a substantial annuity for life, and had shown his earnest purpose by remarking that the greatest assistance he could have now was to be left alone to continue his scientific research. A Banting Research Fund has been founded to which $10,000 of the prize has been contributed toward a $1,000,000 fund, the income of which will forward the work of medical research and scientific study. Dr. Banting has refused all compensation for insulin, which is being made at low cost under license by a pharmaceutical house in Indianapolis. It is estimated that nearly thirty thousand diabetic patients are now under the insulin treatment and no failures have been reported.

The Nobel Prize for physics has been awarded to Robert Andrews Millikan, of Pasadena, Calif., the first scientist to isolate and measure the electron. Dr. Millikan is the director of the Norman Bridge Laboratory of Physics at Pasadena and chairman of the Administrative Council of the California Institute of Technology. He was formerly at the University of Chicago and for years has been identified with the progress of physics in the United States. He has played a large part in the formation and founding of the National Research Council, was most active during the war, and has received honorary degrees from a number of American and foreign universities.

While he was at the University of Chicago in 1910, Dr. Millikan carried out his "oil drop" experiments, which enabled him to isolate an individual ion and to obtain proof of the kinetic theory. As a result of these experiments, he said that he had been able to give tangible demonstration that an electric charge was not a homogeneous something but that it had a definite granular structure.

Subsequently Dr. Millikan advanced the theory that radio-activity was not confined to the radium series alone, but was the general property of all matter, although possessed to a less degree by some substances. In September of this year he established a residence on Pike's Peak to investigate the source of penetrating radiation which has puzzled scientists for years. Previously he had experimented with kites which he sent up with machines that measured rays said to be more powerful than X-rays or the gamma rays of radium. These rays apparently came from space, but not from the sun, as they could be measured at night as well as by day.

In May last, Dr. Millikan prepared a declaration, signed by United States Cabinet officials and leaders in the political, business, scientific, and religious worlds, that there is no antagonism between science and religion.

In 1907, the Nobel Prize in physics was awarded to A. A. Michelson, of Chicago, the prize for medicine to Dr. Carrel in 1912, and in chemistry to T. W. Richards of Harvard, in 1914.

Such recognition honors not only the recipient, but the nation where he has found a congenial home for his laboratory.

TOKYO LETTER

By K. Kashima, 992 Ikebukuro, near Tokyo, Japan

The Earthquake and Chemical Factories

First of all, we are eager to express our sincere thanks for the sympathy and help given by Americans in our recent catastrophe, among whom we can safely reckon were many chemists and members of the Society.

At noon of the first of September a severe earthquake occurred, by which Tokyo, Yokohama, and other cities and villages near Tokyo were largely destroyed. Fire broke out in many places. The commercial and industrial districts to Tokyo and almost the whole of Yokohama were destroyed by fire. In the Honjyo and Fukagawa Districts many chemical factories were almost completely destroyed. There were about 1100 factories in the two districts, employing about 70,000 people. In the Fukagawa District was located the Asano Cement Company, whose products are well known among the cement users. The remaining factories are situated in the suburbs of the city, where the damages were not comparatively large. The total number of factories in the Tokyo Prefecture was about 25,125, employing 152,906 male and 72,391 female workers; 10,913 factories were destroyed and 78,207 people lost their positions. The total damage of the factories is estimated to be about 30 to 40 per cent. According to the investigation of the Agricultural and Commercial Department, the important factories situated outside the burned districts can begin work after two to six months. However, the recovery of these factories is not easy; they must build new buildings and gather workmen, machines, and raw materials. As far as they have money, factories, machines, and raw materials will be obtained, but the expert workmen cannot be obtained with money. The Government intends to lend money for recovering these totally or partly destroyed factories at low interest through the Industrial Bank of Japan or the Agricultural and Industrial Banks. There were many male and female subworkers who were making important contributions to general industry. For example, the labeling of match boxes was conducted by these subworkers. The catastrophe has killed many of these workers and scattered the others into the country. This will greatly hinder the recovery of many of the factories.

Raw and finished cast-iron materials needed in Tokyo factories have been supplied from about two hundred factories in Kawaguchi-machi, near Tokyo. About 50 per cent of these were affected by the disaster and their recovery is now under consideration in the Agricultural and Commercial Department.

The special committee of the Government is now planning the erection of "New Tokyo." As soon as the plans are completed new factories will be built and the sky of the Honjyo and Fukagawa Districts will be blackened with the smoke from the factories' chimneys, as these districts will continue to be factory districts.

The chief damage sustained from the calamity viewed from the standpoint of capitalists is the loss of raw materials and finished products. This loss will be replaced by money. It is not the case from the standpoint of workers. They are now stripped of everything: they cannot work at their trades for they have no factories. They are forced to seek work of whatever kind there is to be found.

Alcohol Industry in Hokkaido

The writer has had a chance to journey through Hokkaido visiting alcohol, beer, and beet sugar factories on the island. The development of civilization on the island is due to contributions of Americans. Travelers perceive American influences in all parts of the island. There are now five alcohol factories—one at Hakodate, one at Kutchan, and the other three near Asahigawa. Potatoes are cultivated in these districts and they are exported after being changed into starch. The potato residue (usually called starch residue and containing about 40 per cent starch), from which starch has been removed, is mainly used as raw material for fermentation, accompanied by corn and oats, etc. Alcohol factories are therefore situated in these districts. The fermentation process is the usual one and the factories are equipped with one or two stills. Almost all the distilled 94 per cent alcohol is diluted with water and sold as "Shôchû" (ardent spirits), a kind of Japanese saké containing about 40 per cent alcohol and consumed on this island and the Kabafuto island. The annual production of 94 per cent alcohol is as follows (unit koku): 100,000 in Honshû, 15,000 in Hokkaido, 100,000 in Taiwan, 10,000 in Chosen—total, 225,000 koku. The annual production of potatoes in Hokkaido is about 151,733,000 kan, in which 61,020,000 kan are used for manufacturing starch.

Soda Industry

It may be safely said that the foundation of chemical industry is a large inorganic chemical industry—that is, of acids and alkalies. The present state of the soda business in this country is not prosperous. The Society of Chemical Industry has published a statement on the soda industry in this country, which contains the following items and their explanations: In general, a sufficient supply of sodium chloride and a low price for caustic soda and soda ash industries are claimed. In the soda ash business this is due to the prevention of sales of soda ash manufactured in foreign countries by the unreasonably low price, the tariff reform for the chemical, and the delivery of a subsidy for the large production in the caustic soda business, to the prevention of importation of foreign soda in excess amounts and the promotion of the research for the utilization of chlorine.

Some supplementary explanations on the industry in this country may be interesting. Before the war we had only two soda ash factories. The Le Blanc method was used and the production was about 2000 tons per year, while the annual consumption of the soda ash was about 30,000 to 35,000 tons. More than 95 per cent of the demand was therefore filled by foreign products, the price being about 2.10 to 2.50 yen per 100 pounds. Then the war broke out and the price was raised to an unreasonable one (maximum 17.85 yen per 100 pounds in December of 1916), and American products took the place of the English.

The investigation committee of the chemical industry decided to build a factory to manufacture soda ash by the ammonia soda process on a scale of 10 tons per day capacity. But this decision was not adopted by the Government. The Asahi Glass Company has therefore built an experimental factory at Tobata-machi, Fukuoka Prefecture, and the work was begun in January, 1917, and was extended to 30 tons per day production in 1922. The Japan Soda Industrial Company has built a factory in Tokuyama-machi, Yamaguchi Prefecture, and also the Taiwan Fertilizer Company at Takao, in Taiwan. The cost of production per 100 pounds is calculated to be 4.79 yen, but this will be decreased to 3.055–2.531 yen. After the armistice these factories were affected by the bad financial conditions. Moreover, at the end of 1921 African natural soda was imported and the price per 100 pounds lowered to 2.70–3.00 yen. The factories were therefore compelled to shut their doors or to decrease their production.

Caustic soda also was manufactured by only two factories before the war, the Le Blanc method being used. The annual consumption of caustic soda before the war was about 15,000 tons, of which about 4000 tons were domestic productions, while the remainder was supplied from abroad, especially from England. After the war, seventeen factories manufactured caustic soda by electrolytic method and eight factories by the Le Blanc method, the total annual production being about 10,000 tons and the consumption about 25,000 tons. The remainder was imported mainly from the United States. After the armistice the price was decreased to an unreasonable one and the caustization of soda ash was carried on as the African soda ash was imported at a low price. Furthermore, when the castic soda was manufactured by the electrolytic method, bleaching powder was produced as the main by-product. These factories are continuing their manufacture on the income from the by-product. But now the production of bleaching powder is over, and another solution must be sought.

Dyestuff Industry

Like other chemical industries, the dyestuff industry in this country has made rapid progress since the war. At the end of 1918 the number of dyestuff factories reached 97, the total capital was 18,642,000 yen (in which the paid-up capital was 13,844,000 yen) and the production in that year was 5,560,000 kin of sulfide dyes, 1,160,000 kin of alizarin dyes, and 480,000 kin of other synthetic dyes, but since 1920 the industry was affected by the bad financial conditions.

The Nippon Senryo Kaisha (Japan Dyestuff Company), in Osaka, was established in 1915 under the protection of the Government and about 10,000,000 yen have been delivered to the company from the Government. This company is the largest and representative of the industry in this country. With the aid of this money the manufacturing processes of the following substances have been completed: 158 kinds of aniline dyes, 148 kinds of intermediates, and 14 assistant reagents, medicine, etc.; of which 45 aniline dyes, 59 intermediates, and 21 assistants, etc., have been placed on the market. The annual manufacturing capacity is 2,200,000 kin of aniline dyes including aniline salt, while the annual consumption of aniline dyes in this country is about 4,700,000 kin.

October 10, 1923

CANADIAN LETTER

By S. J. Cook, 140 Broadway Ave., Ottawa, Canada

New Carbon-Black Regulations

Regulations have recently been established by Order-in-Council permitting the use of natural gas for the manufacture of carbon black in localities where there is no immediate or reasonably prospective market for the gas for domestic or industrial purposes.

If the gas contains gasoline in commercial quantities, the gasoline must be extracted and saved before the gas is burned to carbon black.

If, at some future time, after the factory for the manufacture of carbon black has been established and is in operation, any community or company holding a franchise to supply natural gas to any center of population constructs a pipe line to the wells supplying the carbon black plant, such holder of the franchise shall be entitled to purchase the amount of gas necessary to supply the center of population up to the capacity of the wells, and the carbon black plant will be allowed to burn only the surplus gas for the manufacture of carbon black.

Chemists in Canada

It is estimated that approximately six hundred persons in Canada are practicing the profession of chemistry in one way or another, and recently the Canadian Institute of Chemistry has undertaken to list the names and addresses of these chemists and to record the class of chemical work followed by each. The information obtained will be indexed, and it is expected that much light will be shed on the progress of those industries in which the application of chemical principles has been recognized as having commercial value.

Disintegration of Concrete by Alkali

The action of alkali water on cement and concrete in the prairie provinces is the subject of a progress report received by the Research Council of Canada. A committee formed under the auspices of the Engineering Institute of Canada has been working on the problem for the past two years, and the test blocks of concrete have been deposited in affected areas in Manitoba, Saskatchewan, and Alberta. It will be necessary to allow time for these blocks to disintegrate in order to explore many phases of a question of exceeding importance for the West.

In the past engineers have held that where failures occurred they were due to defective or improperly handled cement. The generally accepted opinion at present, however, is that the disintegration is due to chemical action, causing a softening of the cement. Physical disruption is believed to be caused by crystallization in the pores of the concrete of salts of sodium magnesium or calcium, the sulfates of which are present in alkali ground waters.

This disintegration has become a serious menace to concrete structures, such as building foundations, water pipes and sewers, bridge piers, and culverts. In the western provinces the loss has been estimated at millions of dollars annually. While such structures last many years in eastern Canada, in the West where they come in contact with alkali water they depreciate comparatively rapidly and have to be replaced.

The problem is not confined to the West, for sea water, which contains these salts, is held to be responsible for the failures of concrete docks and other waterfront structures which have been recorded from time to time. It is the work of the committee, therefore, to decide whether the composition of concrete can be modified so as to resist the damage, or whether different building materials will have to be sought.

Provincial authorities in Saskatchewan and Alberta, the city of Winnipeg, and commercial concerns are taking an active interest in the work of the committee, which is under the chairmanship of C. J. Mackenzie, dean of the College of Engineering, University of Saskatchewan.

Improvement in Electrolytic Silver Refining

The Deputy Master of the Royal Mint at Ottawa has recently made public the particulars of an electrolytic process devised by him for the rapid recovery of fine silver from anodes containing 10 to 16 per cent of base metals. A rotating cathode makes possible the use of higher current densities, so that, while the amount of liquid in the cell is less than was formerly employed, the output is considerably greater and the efficiencies obtained average about 78 per cent as against 38 per cent in previous practice.

The new cells are circular, 36 inches in diameter, and the cathodes rotate at a peripheral speed of 40 feet per minute. The current density may be from 75 to 150 amperes per square foot without unduly increasing the temperature of the electrolyte, or fouling it, or increasing the resistance of the cell abnormally. The resistance of the cells does not exceed 1.2 volts at 75 amperes, or 2.5 volts at 150 amperes, per square foot of cathode area. The highest temperature of the electrolyte at 75 amperes is 30° C., and 40° C. at 150 amperes, when running 24 hours per day.

The electrolyte is contained in the annular space between the outer and inner walls of the cells. This space is 8 inches wide and 18 inches deep. The rotation of the cathode keeps the electrolyte well mixed, and prevents any tendency to stratification.

Below are given some comparisons between the old cell and the new type of cell:

	Old Cell	New Cell
Amount of electrolyte in cell	71 imperial gallons	52 imperial gallons
Weight of cathodes in use	285 ounces (renewable every 3 weeks)	311 ounces (permanent; no renewals required)
Anodes in use	5104 ounces	2310 ounces
Current consumption	1.2 volts, 350 amperes	1.2 volts, 400 amperes
Current density per square foot of cathode	13 amperes	75 amperes
Efficiency	38 per cent	78 per cent
Labor required	Stripping cathodes twice daily	No stripping required
Condition of electrolyte	Continually gaining in strength	Constant
Agitation of electrolyte	By mechanically driven stirrers (not thorough)	By rotation of cathode (thorough)
Output of silver per cell per hour	17.30 ounces	40.30 ounces

Sugar Beet Industry for Manitoba

Experiments in the growing of sugar beets in Manitoba this year have so far proved satisfactory and strengthen the belief that the American company which is behind them will next year go ahead with its plans for planting from 10,000 to 12,000 acres of sugar beets and establishing a plant for the manufacture of beet sugar in Winnipeg.

Big Pulp Mill to Use Straw

Erection of one pulp mill in the vicinity of Winnipeg in the near future, with the prospect of several others should the first prove a success, was the hope expressed by M. Dollfus, London, managing director of the De Vains Pulp Company, who, with Sir Frederick Becker, chairman of the company, recently visited in Winnipeg.

The plant will be operated under a new system of pulp production in which straw is the chief constituent, Winnipeg having been considered an excellent location for such an industry in view of the large quantities available from the prairies. Any straw except that of rye can be used, it was stated. Previous processes had cooked the fiber to a jelly and made it of little use in paper manufacture. By the De Vains plan the fiber is kept in good condition throughout and pulp produced by it is slightly cheaper than that made from wood.

The visitors represented a group of amalgamated companies operating in different European countries and in Java, where a large mill is in operation.

October 24, 1923

PARIS LETTER

By Charles Lormand, 4 Avenue de l'Observatoire, Paris, France

Congress of Industrial Chemistry

The Third Congress of Industrial Chemistry has just closed. Among the foreign delegates who assisted at this Congress we have the pleasure of mentioning C. H. Herty, W. A. Noyes, F. E. Breithut, and E. S. Chapin, delegates from the American Chemical Society.

The business sessions of the Congress, presided over by several members of the French Government, were devoted to three general conferences.

In the first, M. Menozzi, director of the Royal High School of Agriculture of Milan, gave the history of the methods employed in the analysis of the soil, and showed especially the conditions under which the elements composing the vegetables (phosphoric acid, potash, nitrogen, etc.) should be dissolved before being assimilated by the plant. He told of successful work in Germany which permitted determining minimum quantities of phosphoric acid, nitrogen, potash, and calcium which would permit the cultivation of the sugar beet. The different questions concerning the reaction of the soil and the small quantities of toxic substances for the plants were explained by the lecturer, who concluded in saying that the analysis of the soil should be made before undertaking its cultivation and that the results obtained would permit the choosing of fertilizer or necessary amendments.

In the second conference M. Lindet described the progress made in France on the reconstruction of sugar works and distilleries destroyed during the war. In 1924 France possessed 210 active sugar factories, producing a total of 785,550 tons of sugar. This figure is clearly a decrease from the figures of 1900–1902 when the production reached 1,160,110 tons.

The production of sugar in Germany, which in 1902 was about 2,139,960 tons, in 1914 was about 2,715,270 tons. In Austria the production, which was 1,187,200 tons in 1902, reached 1,692,000 tons in 1914.

The consumption of sugar in France in 1902 was around 453,000 tons, and reached 710,000 tons in 1914. It can be seen that at this period the production was practically equal to the consumption. During the war 148 of our factories, about two-thirds, were destroyed. The production in 1918 was only 110,000 tons. It is seen that in reality the regions of the cultivation of the sugar beet are the regions of the North, the Aisne and of Pas-de-Calais, all regions which were invaded. During the same time, Germany and Austria kept their total production of sugar, and the production of cane sugar increased fourfold, since the world production of cane sugar, which was three millions of tons in 1899, increased to twelve millions of tons in 1920. The 148 factories which were destroyed were not all rebuilt. One hundred and ten were restored as before. The others were united in groups of two, three, and even more. They commenced to operate in 1921. The total production, which was 110,000 tons in 1918, increased regularly from this time. It reached 445,000 tons last year and it is hoped that it will reach 480,000 tons this year. This figure is still far from the 700,000 tons of annual consumption. Efforts have been made to develop the cultivation of the sugar beet in other regions than the north of France.

In the matter of distilleries, of which there were 300 in France, 150 have been destroyed. The reconstruction of these distilleries is more slow, delays being necessary for the study of and adjusting problems concerning the national fuel and industrial alcohol.

As for the breweries, out of 2570, 1767 were destroyed. Most of these have been rebuilt, but it is probable that these cannot be wholly reconstructed for the consumption of beer in France has fallen with the gain in that of wine.

In the last conference Sir John Russell, director of the laboratories of Rothamsted, described the influence of microörganisms on the fertility of the soil. Sir John Russell explained in an authoritative manner the formation of the humus through mechanical and chemical disintegration of the residue of vegetation. He has studied the destruction of phenol compounds by bacteria, the refuse from the dead plant, and which were toxic for the young plant, as well as the relation existing between the bacterial composition of the soil and its content of carbohydrates and nitrogen compounds in the organic or mineral form.

The speaker explained the methods used at Rothamsted for studying microörganisms: (1) separation, enumeration, according to the methods usually employed in bacteriology; (2) physiological grouping; (3) statistical method. With this last method for 366 consecutive days a lot of earth fertilized with farm manure was studied. The number of bacteria varied continually with no relation between these variations and those of the atmosphere (temperature, humidity, etc.). Nevertheless, it was noticed that the number of bacteria was greater in the spring and in the autumn than in summer and winter. The protozoa varied the same as the bacteria, but there was always an inverse ratio between the number of protozoa and those of bacteria—that is, a high number of protozoa corresponded with a weak number of bacteria, and vice versa. The inoculation of the protozoa in the sterile soil confirmed these facts. It is now shown that the number of protozoa regulates the number of bacteria.

In a parallel study of the variations of nitrates in the soil, it is established that these variations are independent of the atmospheric conditions or of the vegetation, but that it is possible to unite these two phenomena—that is, to regulate the production of nitrates by the fixation of the nitrogen of the air through the bacteria in increasing the number of bacteria. This can be realized with partial sterilization. This sterilization can be effected with different bodies, as I have pointed out in previous letters. M. Truffaut, in France, uses calcium sulfate with success. The results obtained are already in the power of practical agriculture. Hydrocarbons and certain derivatives of coal have also been used. In England, nitrogen fertilizers have a better market than antiseptics; this is because gypsum, the raw material in the manufacture of calcium sulfate, is not very abundant in England and that the derivatives of coal are used in the dyestuffs industry. In countries such as France or America, where gypsum is found in abundance, calcium sulfide is used for the sterilization of the soil, and consequently the fixation of the nitrogen, to compete with nitrogen products. There has also been a series of investigations on the antiseptic derivatives of coal tar. There is no doubt but that, among the intermediate products of the manufacture of dyes or in the wastes of this manufacture, there may be found substances possessing sterilizing properties for the soil.

Aside from these conferences, the Congress has collected numerous communications, all of which are very interesting. I would particularly mention that of Georges Claude, who has combined in the same fertilizer ammonia and potash. For this he uses sylvite, which is the mineral of our Alsatian potash and which is composed of a mixture of potassium and sodium chlorides. In treating the sylvite with carbon dioxide sodium is precipitated in the form of a carbonate, whereas the potassium chloride remains dissolved with the ammonium chloride which will be formed in the reaction of sodium chloride on the carbonate of ammonium and which can be separated by cooling to 5° C. by means of the expansion of liquid ammonia.

The advantages of the Claude process are (1) the substitution in the sylvite of harmful sodium chloride for ammonium chloride, a nitrogen fertilizer, (2) the transformation of ammonia in fertilizer with the aid of chloride coming from the sylvite, (3) the production of sodium carbonate with the aid of the sodium chloride contained in this sylvite, the sodium chloride in the sylvite having no value. This solution of the problem of nitrogen and potassium fertilizers sounds very well, but it supposes that the ammonium chloride has the same value as the sulfate. With equal weights of nitrogen, there would be equivalence between the chloride and the sulfate, and as the nitrogen chloride is less expensive than the nitrogen sulfate, it is the nitrogen chloride that in the end should be employed.

I would like to mention here that M. Prianicknikof has recently presented to the Academy of Science a comparative study of the fixation of nitric nitrogen and ammoniacal nitrogen. In the comparative cultivation and with equal weights of nitrogen, the organic nitrogen fixed by maize is 844 using calcium nitrate, but it increases to 935 by using a mixture of ammonium chloride and calcium carbonate, which confirms the superiority of the ammoniacal nitrogen over the nitric nitrogen. The ammoniacal salts can be arranged as follows in order of assimilability: the most assimilable is ammonium carbonate, then the phosphate, and finally the chloride and the sulfate.

This communication confirms the views set forth by M. Claude. He has also studied the problem of phosphates. He described an installation producing 3 tons per day of finely pulverized phosphates, since it is known that at the present time it is possible to replace superphosphates by very finely divided natural phosphates. M. Claude ground the phosphate mechanically, which was then treated with a current of air. The largest particles were deposited. In the end only a suspension of extremely fine dust remained. The air current containing this dust was subjected to electrical precipitation by the Cottrell process and the extremely fine dust obtained was ready for agricultural uses.

Hydrogeological Study in Madagascar

I should like to speak of the various other interesting problems taken up at the Congress, but I should mention the return to France of Professor Moureu, whom I have just had the pleasure of interviewing. M. Moureu has been studying hydrogeological problems on the Island of Madagascar and the Island of the Réunion.

There exist, particularly in Madagascar, in the volcanic region of Antsirabé, sources of bicarbonate of soda and calcium waters analogous with our waters from the Vichy basin. These waters have been examined by M. Moureu and they have been found to possess the same therapeutic properties as the waters of Vichy.

M. Moureu has also studied the numerous sources of carbonic acid gas which they call the "flower of the soil" in these regions. He is going to follow this with studies on the very interesting rare gases, and especially on the possibilities of obtaining large quantities of helium. It is known that Madagascar is rich in radium minerals. These minerals are as yet little used, and it is thought that they may rival the minerals of the Belgian Congo.

October 31, 1923

GERMAN LETTER

By Max Hobein and Ludwig Kalb, Ebenhausen bei Munchen, Germany

Combustion in the Diesel Motor

From the abundance of material which was offered by the Diesel Motor Section of the German Engineers' Society, in Berlin, which gives evidence of the importance that the Diesel motor has attained in the last few years, two addresses may be briefly mentioned.

In "Fuels and Their Combustion in the Diesel Engine," Chief Engineer Alt, of Kiel, points out that the atomized fuel can be ignited directly in the Diesel engine in the fluid form. The previously accepted belief that gasification first had to take place must be given up. The behavior of fuels depends, then, only on their chemical composition, which determines their kindling temperature. For smooth burning without the formation of soot Herr Alt even recommends that gasification before ignition be prevented if possible.

In "Increase in Efficiency by the Four-Cycle Diesel Motor," Dr. Riehm, of Augsburg, describes interesting experiments. In order to increase the available piston pressure neither the fuel nor the amount of air can be made greater. In the first case the rapidly increasing heat requirements soon set a limit to the process, so that it is only temporarily useful. In the second case the increase in heat requirements is negligible. The increased amount of air is allowed to enter the cylinder in such a manner that the fresh air sucked in is condensed before entering. Without noticeable increase of fuel consumption the efficiency can be made 30 to 40 per cent greater. A further gain would be accomplished if it were possible to use the energy of the exhaust gases for condensing the air by coupling the blast with an exhaust turbine, as has already been successfully done with airplane motors.

Mist Explosions

Professor Haber, the well-known discoverer of the ammonia process named after him, has in *Zeitschrift für angewandte Chemie* published an investigation carried out with Herr Wolff at the Kaiser-Wilhelm Institute for Physical Chemistry, in Berlin.

While the explosive limits, the rate of transmission of the explosion, and the resulting smoke gases in gas-forming, homogeneous mixtures of combustible materials have been much studied, concerning the nonhomogeneous, combustible mist these things are not known. Mist explosions can play a part in motor explosions caused by high-boiling fuels, for it does not matter whether the heating through compression and from the walls is sufficient to vaporize completely before igniting the fuel introduced in the form of droplets.

In carrying out the experiment the production of a uniform, explosive stream of mist was necessary, which was connected with the flue and from which the apparatus was filled when necessary. This was successful, not because of the manner of atomization, but because of the rapid cooling of the heated mixture of the combustible gases with air. Mist from petroleum (180° to 220° C.) or from tetralin or quinoline was studied.

Three results of this work may be mentioned:

1—The lower explosive limit—that is, the least proportion of mixture to combustible substance which is necessary for the explosion to take place is proved to be independent of whether the fuel exists nonhomogeneous in the form of droplets, or homogeneous in gas form.

2—While homogeneous gas-air mixtures burn quite completely to carbon dioxide and steam as long as stoichiometric excess of oxygen is present in the mixture, the mist requires a considerable excess of oxygen, and the larger the particles are the greater excess is necessary. Because of this lesser ability of the mist for complete combustion it is more efficient to use the fuel in the explosion motor in the form of a homogeneous gas-air mixture.

3—The speed of explosion in the mist is less than in the gas-air mixture—which is a further advantage of the homogeneous gas-air mixture.

Relation between Composition and Chemical Resistivity and of Glasses

Professor Keppeler, of Hanover, discussed this subject at the meeting of the German Ceramic Association in Blankenburg. He brought proof for the theory that the chemical susceptibility of glasses to attack is attributable to the solubility of the single components, especially the oxide. The tinge of coating consists mostly of a thin layer of soda crystals, as can be seen through microscopical analysis. Sodium is dissolved out of the glass by water and is converted into carbonate by the carbon dioxide of the air. Likewise, the devitrification of old glass is due, not to crystallization processes (structural changes) but to hydrolysis. While it was possible to produce practically insoluble calcium glass, this could not be done after the introduction of strontium or barium in any proportions.

Sulfuric and Hydrochloric Acids from Sulfurous Acid and Chlorine

The chemical change according to the equation

$$SO_2 + Cl_2 + 2H_2O = H_2SO_4 + 2HCl$$

can—with the synthesis of hydrochloric acid from chlorine and hydrogen—gain new significance in Germany, as in the chlorine-alkali industry a considerable excess of chlorine has been observed since the war. Professor Neumann, of the Technological Institute of the University of Breslau, has, in coöperation with Herr Wilczewski, devoted an exhaustive experimental study to the foregoing reaction, concerning which he has written in *Zeitschrift für angewandte Chemie.* He includes suggestions for the practical carrying out of the process in a system of acid-proof trickling towers, for which he recommends the apparatus designed by Tobler (U. S. Patent 1,332,581).

The results of the investigation may be summarized as follows: The reaction between sulfur dioxide and chlorine in the presence of water takes place quantitatively. Therefore, at first acid fumes which are not easily condensed result. The sulfuric acid fumes are more difficult to condense than hydrochloric acid fumes. In practice the reaction is allowed to proceed in trickling towers in which, instead of water, preferably, concentrated hydrochloric acid is introduced. With increasing concentration of sulfuric acid the hydrochloric content of the mixture decreases and disappears almost completely upon reaching a specific gravity of 1.6. The concentrations of sulfuric acid attainable are the same as those of the chamber or glover acid (66 to 88 per cent). The sulfuric acid produced can be freed from dissolved sulfur dioxide (or chlorine) by a stream of air easily and almost without any remainder. It is not possible to produce sulfur trioxide according to the equation $SO_2 + Cl_2 + H_2O = SO_3 + 2HCl$.

October 10, 1923

BOOK REVIEWS

The Chemical Resistance of Engineering Materials. By M. L. Hamlin and F. M. Turner, Jr. 276 pp. The Chemical Catalog Co., Inc., New York, 1923. Price, $5.00.

In the preface the authors have limited their task by waiving the intention of making an exhaustive treatise. Notwithstanding the self-imposed limitations of scope their undertaking is ambitious.

Trying sincerely to give the divisions of their subject proper perspective, they have properly given sulfuric acid the center of the stage by devoting about 15 per cent of their total space to its reactions upon most commercial structural materials, particularly metals and metal alloys. They follow this with briefer but similar treatment of the other commercial acids—hydrochloric, nitric, acetic, etc.—giving a little space to less important organic acids—citric, malic, picric, etc.

At the end of the third chapter, Other Acids and Metals, are a few pages on the general subject of corrosion. While this subject unquestionably belongs in a treatise of this kind, the average reader would hardly expect to find it subordinated to the reactions of commercial acids. It would seem logical to devote a main division to this subject, introductory to the more specific problems.

The fourth division of the work, Acids and Non-Metallic Materials, seems to be logically covered within the scope of the undertaking. The treatment of Bases and Alkaline Salts and Neutral Substances is very sketchy. The chapter on Selection of Material for Specific Equipment is bravely undertaken, and will be appreciated by most engineers. The table of materials for evaporators will be useful, as will also the table given of materials for pumps. A special chapter on concrete contains much condensed information. Each chapter is followed by an extensive bibliography.

The book has appendixes occupying about 65 pages, containing much handbook data, some of which is certainly not to be found in existing handbooks.

Withal, the work serves a need. It can be criticized on the ground of judgment used in the disposition of space and emphasis. With some rearrangements and additions of quantitative data, clothed in a limp leather binding, embossed with gold letters, and printed on India paper, the names of Hamlin and Turner could go down the decades in the esteem of engineers along with those of Kent and Foster.

F. W. Willard

Die Ole und Fette in der Textilindustrie. By Dr. Herbig. Vol. III of Monographien aus dem Gebiete der Fett-Chemie. 301 pages. Published by K. H. Bauer, Stuttgart, 1923.

The scope of this book includes the determinative factors of the fats, oils, and soaps employed in the textile industry, with information on the substances found in them as adulterants or impurities, and also the commercially reliable quantitative methods for determining the percentage values of each.

The text is simple and straightforward, and ought to offer no difficulty to those having a moderate knowledge of German. The different sections of the text are clearly and logically arranged, but a more careful breaking up into definite chapters, with an analytical table of contents to each chapter, would have added much to convenience in consulting the work. Altogether, however, the book is a valuable one, and deserves use.

Frederick S. Beattie

The Causes and Prevention of Corrosion. By Alan A. Pollitt. 222 pages. Ernest Benn, Ltd., London, 1923. Price 25 s. D. Van Nostrand Co., New York, 1923. Price, $6.50.

This book offers a concise, open-minded, and reasonably complete presentation of the various factors involved in the corrosion of iron and steel, though there is little novelty in the subject matter or its presentation. The corrosion of nonferrous alloys is not discussed except in the case of brass condenser tubes.

In the sections on the theory of corrosion the author pays more attention to the results of extensive work in this country than have many other English writers on this subject, but he is nevertheless not quite willing to accept the "electrolytic" theory. As a result, the theoretical discussions are rather inconclusive. The author also helps to perpetuate the common misconceptions and haziness as to the mechanism of galvanic action and the accelerating effect of impurities in metals.

Practically all the section on the corrosion of condenser tubes is quoted directly from the excellent "Notes" of Bengough on the work of the Corrosion Research Committee of the Institute of Metals. This was published last year, but is not generally available in this country.

The sections on various types of protective coatings are probably the best portions of the book, representing concise presentations of the more important facts regarding nearly all the protective substances or processes now in commercial use.

The rather extensive discussion (25 pages) of boiler water softening scarcely seems necessary in a book on corrosion.

While the book is dated June, 1923, a number of important contributions during the preceding year were apparently not considered in writing certain sections. This is also true of the excellent work of the A. S. T. M. on the effect of copper in sheet steel on atmospheric corrosion, which has been covered in committee reports for several years.

The book is well printed on an excellent quality of coated paper, which probably accounts for the rather high price. It is, however, a book which could very profitably be read by anyone wishing to acquire a reliable bird's-eye view of the whole field within reasonable limits of time and space.

Robert E. Wilson

Gas Manufacture. By W. B. Davidson. 464 pages. 147 figures. Longmans, Green & Co., New York, 1923. Price, $7.00.

This book is planned to give the student of gas manufacture an insight into fundamental principles, particularly the chemical and physical principles underlying the industry's operations. The author well states his approach to the subject in the preface when he says: "The chemical aspect is in the forefront, and the mechanical more or less in the background."

The work, being written by a British engineer, of course deals largely with manufacturing conditions and methods of Great Britain, but most of the volume loses but little for the American engineer as a result. Only in such sections as those discussing the regulation of gas by public officials and the details of testing methods required will the American reader need to be on his guard lest he be led away from standard American practices. Most of the rest of the book is directly applicable to conditions in this country.

A careful examination of the volume leads one to believe that it has been written as a textbook. The material is selected because of its general significance for the industry as a whole, and is pedagogically well organized and clearly presented. It is a surprise, therefore, to turn to the title page of the work and find the author listed as a consulting chemical engineer, with other connections which give no hint of college or university affiliation. But this professorial attitude of the author has had a fortunate result, for it has produced a well-balanced and usable work, which is not always the case when the so-called "practical" engineer turns author.

The title of the volume is somewhat deceptive, for it goes far beyond a discussion of the manufacture of gas. The work is in fact roughly divided—20 per cent on fundamental chemistry; 40 per cent on manufacturing methods, equipment, and by-products; 25 per cent on distribution of gas and its utilization; and 15 per cent on laboratory testing methods, official regulations, and public relations questions.

The book is splendidly prepared mechanically, both accurate and attractive in type forms, with good illustrations and binding. It deserves a place in every gas engineer's library, and will find cordial welcome among the professors of chemical engineering and gas engineering. Although not altogether suitable as a textbook for American students, it certainly will be a very valuable reference book for use in their classes.

R. S. McBride

Report of the Committee of the Privy Council for Scientific and Industrial Research for the Year 1922–23. 141 pages. H. M. Stationery Office, London, 1923. Price, 4 s net.

The British Government's scheme for promotion of scientific and industrial research has now been in operation for eight years. A Committee of the Privy Council, responsible for the expenditure of funds provided for this purpose, and an Advisory Council, to make recommendations regarding researches to be undertaken and grants to be made, were appointed in 1915. The Department of Scientific and Industrial Research was created in the following year to carry out the plan; and to this the National Physical Laboratory and the Geological Survey were transferred in 1918–19. A trust fund of a million pounds was initially provided by Parliament for subsidizing industrial research associations, and annual appropriations have been made for the work of the department and its institutions. The present report deals with the activities of all these research agencies during the last fiscal year.

Twenty-four research associations have now been approved in as many industries, flour-milling having been added last year. Within certain limits, they generally receive grants from the Million Fund, for five years, equal to the amounts subscribed by their members. Some of these associations are now approaching or have reached the end of their grant periods. An important decision has been reached to consider each application for extension on its own merits, and to make further grants only if it is shown that the industry is unable immediately to shoulder the entire financial responsibility for its research association but can in all probability provide an effective income for its complete support within another five years.

The report includes a summary of investigations completed or in progress directly under special boards and committees of the department dealing with problems relating to fuel, food, forest products, building materials, adhesives, gas cylinders, lubrication and current meters, as well as in the National Physical Laboratory. An interesting account is given of the work of five coördinating research boards for physics, chemistry, engineering, radio, and fabrics, originally established in 1920 to control fundamental scientific research in connection with the fighting services, but now also correlating it with similar work under various civilian departments and industrial research associations. Developments in the organization of research in the British Colonies are noted in one of the appendixes.

J. Daniel Thompson

Gelatin in Photography. Vol. I. By S. E. Sheppard. 22 × 15 cm. 263 pages. D. Van Nostrand Co., New York, 1923. Price, $2.50.

Unsuccessful attempts to use gelatin in photography were made by Mepce in 1847, Poitevin in 1850, and Gaudin in 1853. Norris in 1856 was the first to use gelatin successfully in connection with collodion dry plates. Maddox in 1871 was the discoverer of what has developed into the modern gelatino-bromide emulsion. In 1873 the preparation of a gelatin film emulsion in a practical form was accomplished successfully by Kennett. In 1883 the first isochromatic plates were placed on sale by Tailfer. Eastman introduced the film in 1884 and the nitrocellulose film in 1889.

The subject of gelatin in photography is so large that this volume deals only with the historical, manufacturing, and analytical aspects of gelatin, the technology of the manufacture and testing being discussed primarily with a view to the improvement of gelatin as a photographic raw material. It is in this respect that this volume differs from the more comprehensive ones by Bogue and by Alexander. The subject is presented under the general headings: A History of the Applications of Gelatin in Photography; The Manufacture, Technochemistry, and General Properties of Gelatin; The Analytical and Constitutional Chemistry of Gelatin.

Hatschek's method for determining the setting point is very interesting (p. 202). Among special instruments devised by the author are the jelly-strength testing machine (p. 213), and the turbidimeter (p. 220). For exact moisture determinations the method of Hulett is recommended (p. 113). "Apart from physical and colloid-chemical characteristics, there are certain special requirements for photographic gelatins. They should give clear and nearly neutral solutions; the moisture content should not be above 20 per cent, and lower for 'soft' gelatins; and the ash should not exceed 2 per cent" (p. 117). Bases and heavy metals should not be present in the ash in more than mere traces as they are harmful to photographic emulsions. Sulfates and chlorides should also be low.

The book is a good one, but is handicapped by the fact that what we really want to read is the second volume.

Wilder D. Bancroft

Farberei- und Textilchemische Untersuchungen. By Paul Heermann. x + 370 pages. Julius Springer, Berlin, 1923. Price, $2.50.

This manual might adequately be described as a manual of the tests for purity of all substances employed in the textile industries, beginning with indicators, standard solutions, and the substances from which these are prepared, and going on through spinning fibers, water, heavy chemicals, tanning agents, fats and oils, soaps, starches, gums, etc., natural dyestuffs, weighters, determination of dyes upon the fiber, tests for fastness upon the fiber, and an appendix containing various tables. Besides methods for the quantitative determination of the percentage of the substance itself in samples tested, similar tests are also given, qualitative and quantitative, for the impurities which may be present.

The text is well arranged, but with the usual defect of too massive blocks of print, without sufficient paragraphing to make rapid consultation of the work easy. This defect, however, is common in Continental works, and may perhaps better be ascribed to a general difference in mental attitude toward such matters.

The treatment is full but concise, and is quite evidently very thorough. It is difficult, off-hand, to find any topic which properly comes within the range of the subject that has not been fully taken up.

Frederick S. Beattie

Étude sur la tannerie et les Industries connexes au Maroc. By CH ZIEGLER. 122 pages. 28 plates. 13 x 22 cm. La Chaussure Francaise, Paris, 1923. Price, 7 fr. 50.

This little volume presents an account of a study of the tanning industry in Morocco. This study embraces the whole industry from the sources of the raw materials, both skins and tannins, to the manufacture of the finished leather into slippers and similar articles. The raw materials, all of native origin, and the processes of tanning, all of primitive nature, are treated in great detail. The purpose of the publication seems to be mainly the fostering of an interest in the activities of this French dependency rather than the furthering of our scientific knowledge concerning leather. There are, however, some points of interest to the leather chemist in the methods of tanning employed, which are empirically developed to meet the peculiar circumstances and prevailing climatic conditions. Liming for three weeks and then deliming for two months seems a startling procedure, especially in such a climate, and yet the Moroccan tanner appears to get away with it.

If a few chemical and bacteriological examinations were reported in connection with Mr. Ziegler's study, the value of the publication would be immeasurably increased from the scientist's point of view. As it stands, despite the interesting nature and very readable method in which the subject is presented, it is doubtful whether the book really belongs in a chemical library.

THOMAS BLACKADDER

Kent's Mechanical Engineers' Handbook. ROBERT T. KENT, Editor-in-Chief. 10th edition. 2247 pages. John Wiley & Sons, Inc., New York, 1923. Price, $7.00.

It is very difficult to review adequately such a comprehensive volume as "Kent's Mechanical Engineers' Handbook." However, it does not require the ordinary treatment, since it has been the handmaid of the engineer for many years and because the members of the engineering and scientific professions have been acquainted with its context and have recognized it as one of the most authoritative sources of information. The former editions have been well received and it is predicted that the last edition will meet with a like reception. In many respects the new edition is a marked improvement over former editions. This is true because a great deal of the material has been entirely rewritten, much new material has been added, and changes have been made in classification and arrangement of material.

There are certain undesirable features in the present edition. It is regrettable that in the effort to keep the volume within a small compass some of the figures and plates were produced on such a small scale as to make it difficult to read them with correctness and facility. The work can be questioned as to the relative amount of space given to different topics. For instance, three and a half pages are devoted to windmills and less than half a page to railway cars. This is a serious error in both instances as windmills are not of sufficient engineering and economic importance to devote that amount of space to, and railway cars are of such prime importance to transportation that they deserve a much better treatment.

Likewise with the locomotive and railway cars. A great deal of space was given to the locomotive and correctly so—but it is not so overwhelmingly more important than the railway cars as represented by the difference in space allotted. The design of railway cars is equally important and difficult as that of locomotives and not a word has been said concerning it. It would have been far better to have omitted some of the questionable empirical formulas for design of certain locomotive parts and utilized the space by giving sound principles of and formulas for car design. It appears hardly justifiable to give data on the waste of fuel in locomotive operation from an article published in 1894. In the first place, there is more current information, and, second, such information is not applicable to modern conditions.

The treatment of smoke prevention is inadequate. Certainly, some reference should have been given relating to ordinances, methods of rating amount of smoke, and the amount of loss due to smoke. It is unfortunate that in the section on Industrial Buildings the important function of the flow sheet as a prerequisite to logical factory design and lay-out was not mentioned. The discussion of arrangement of machinery is faulty in that it is not adequately discussed, and, furthermore, many would take grave issue with the statement "for low cost it is better to group machines by classes."

Notwithstanding the unfavorable references made, the reviewer realizes that the new edition is a marked improvement over former editions, and feels therefore that the editor, his associates, and publishers have rendered a distinct service to engineers and to industry by making available this revised edition of a handbook that successfully has met their requirements for many years.

L. W. WALLACE

NEW BOOKS

Auszüge aus der Literatur der Zellstoff- und Paperfabrikation. I. Chemischer Teil. II. Mechanischer Teil. Verein der Zellstoff- und Papier Chemiker und Ingenieure. 36 and 48 pp. Otto Elsner, Berlin

Bibliography of Periodical Publications on Papermaking and Allied Subjects during 1922. 37 pp. Price, 5 s Papermakers' Association of Great Britain and Ireland, London.

Blasting with High Explosives. W. GERARD BOULTON. 108 pp. Price, 5 s. Sir Isaac Pitman & Sons, Ltd , London.

Bulletin of the Imperial Institute. Report on the Operations of the Imperial Institute. Vol. 21. No. 1, 289 pp. Price, 3 s. 6 d. John Murray, London.

Fabrication des Colles et Gélatines, Traitement Industriel des Animaux Abbatus. VICTOR CAMBON. 268 pp. Illustrated. Price, 18 fr. Dunod, Paris.

Genesis of Petroleum. P. E. SPIELMANN. 72 pp. Price, 5 s. E. Benn, Ltd., London.

Handbook of Petroleum, Asphalt, and Natural Gas. ROY CROSS. Bulletin No. 16 of Kansas City Testing Laboratory. 650 pp. Price, $7.50 Kansas City Testing Laboratory, Kansas City, Mo.

Handbook on Rubber Uses and Their Development. 162 pp. Rubber Growers' Association, Inc., London.

Industrial History. HARRY B. SMITH. 305 pp. Illustrations. Price, $1.40. The Macmillan Co., New York.

Kolloide in der Technik. IX. Wissenschaftliche Forschungsberichte. RAPHAEL ED. LIESEGANG. 157 pp. Theodor Steinkopff, Dresden and Leipsig.

Leather Trades' Year Book, 1923. J. GORDON PARKER. 216 pp. Price, 6 s. 6 d. Leather Trades' Year Book, London.

Manufacture of Nitric Acid and Nitrates. ALLIN COTTRELL. 454 pp. Price, 36 s. Gurney & Jackson, London.

Nickel Ores. W. G. RUMBOLD. Monographs on Mineral Resources with Special Reference to the British Empire. Mineral Resources Committee of the Imperial Institute. 81 pp. Price, 5 s. John Murray, London.

Practical Chemistry. H. B. DUNNICLIFF. 280 pp. Price, 5 s. Macmillan & Co., Ltd , London.

Preparation of Perfumes and Cosmetics. J. P. DURVELLE 420 pp. Price, 21 s. Scott, Greenwood & Son, London.

Rubber Latex and Its Industrial Importance. A. VAN ROSSEM. International Association for Rubber Cultivation in the Netherland Indies. 34 pp. Netherland Government Rubber Institute, Delft.

Source and Influence of Impurities in 80:20 Cupro-Nickel. C. BLAZEY. Munitions Supply Board, Australia. 56 pp. Australian Commissioner's Office, New York.

Steaming of Wigan Arley Coal in Vertical Gas Retorts. Technical Paper No. 8. FUEL RESEARCH BOARD. Department of Scientific and Industrial Research. 12 pp. Price, 9 d. H. M. Stationery Office, London.

Structure of the Atom. E. N. DA C. ANDRADE. 314 pp. Price, 16 s. G. Bell & Sons, Ltd., London.

Technical Reports, 1921-1922. Munitions Supply Board, Australia. 34 pp. Australian Commissioner's Office, New York.

Textile Chemistry. F. G. COOPER. 235 pp. Price, $5.00 E. P. Dutton & Co., New York.

Treatise on General and Industrial Organic Chemistry. Part II. E. MOLINARI 2nd edition, *translated* by T. H POPE. 440 pp. Price, 30 s. J. & A. Churchill, London.

GOVERNMENT PUBLICATIONS

Commerce Reports—October

Notice—*Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington, D. C. The regular subscription rate for these Commerce Reports mailed weekly is $3.00 per year (10 cents per single copy), payable in advance to the Superintendent of Documents, Government Printing Office, Washington, D. C.*

It is claimed that methods have been perfected by which commercial products can be obtained from the Athabaska tar sands found in the Province of Alberta, Canada. Two processes have been developed, one for the separation of **oils** and the other for the extraction of **asphalt.** (P. 16)

The **fertilizer** industry of the Netherlands is reviewed, and statistics are given showing the imports and exports of artificial fertilizers. (Pp. 19–20)

Export and import statistics for **coal-tar products** are given for the Netherlands, there having been a rather rapid and otherwise notable development in the manufacture and exportation of these products during the past two years. (Pp. 20–1)

Mineral turpentine, which sells for about half the price for vegetable turpentine, is the variety most widely used in the paint trade in Shanghai. (P. 21)

The August trade of the United States in **chemicals** and allied products is reviewed. Although the exports recorded a gain of 25 per cent as compared with August, 1922, there was a decided drop from the previous months of 1923. On the other hand, the imports during August, 1923, not only gained over August, 1922, but also over the preceding month. The exports of chemicals and allied products had an aggregate value of $11,943,966, while the imports totaled $16,045,609. (Pp. 90–1)

The Chilean Government, in order to finance the 1923 budget, has proposed the sale of certain Government **nitrate** lands. (P. 91)

The total **lignite** resources of Italy have been estimated at 295,189,000 metric tons. (P. 105)

The opening meeting of the Royal Commission to inquire into the **pulpwood** resources of Canada and to determine the advisability of restricting or prohibiting the exportation of pulpwood from Canada was held on September 10 at Ottawa. It is probable that hearings will be held from coast to coast. (P. 119)

The dyestuffs market of the Irish Free State is now open to American producers on equal terms with all others. (P. 119)

In accordance with an Imperial Ordinance promulgated in Japan, effective September 17, the following **commodities** have been **exempted** from **import duties** until March 31, 1924; mineral oils; sengen root; boric acid; tartaric acid; bicarbonate of soda; salicylate of soda; peroxide of hydrogen; alum; chloroform; iodoform; milk sugar; antipyrin; santonin; carbonate of creosote; carbonate of guaicol; pepsin; and drugs, chemicals, and medicines. (P. 120)

A recent French decree modifies the import duties, generally by way of reductions, on **cottonseed oil** and **sulfuric acid.** (P. 120)

The Governor General of the Union of South Africa has proclaimed a **rebate** in the **import duty** on the following products: turpentine, vegetable or mineral, for use in the manufacture of paints, varnishes, and polishes; eucalyptus, pine, and other oils, for use in connection with the extraction of gold and other minerals by the flotation process; soy-bean, citronella, and mirbane oils, for use in the soap-making industry; waxes for use in the manufacture of polishes; and linseed oil, raw, for use in the manufacture of paints for resale. (P. 121)

Orders for French **heavy chemicals** are improving continually and are now equaling production. The large companies are busy because of the failure of German deliveries. Good business is being done in mineral acids. Secondary chemical industries are improving, with good demand for their products, especially from glass-makers and tanners. (P. 141)

The **paint** and **varnish** market in Chile is reviewed. It is pointed out that Chile offers a good market for paints and varnishes, but that competition is keen. In proportion to the size of the country and its small population, relatively large quantities are consumed annually in a variety of ways, and statistics are given showing the principal sources of the various paints and varnishes imported into Chile. (P. 161)

A report from Berlin is to the effect that representatives of the Government, agriculturists, and the nitrogen industry have made an agreement whereby the price of **nitrogen** is fixed on the basis of the price of rye, the price of 140 kilos of rye being taken as that of 100 kilos of sulfate of ammonia. The price of calcium cyanamide is to be fixed at eight-ninths and that of soda nitrate at one and one-ninth the price of sulfate of ammonia. (P. 161)

Owing to the heavy sales during the last few months, it is announced that the product of nearly all the German **potash** works is exhausted. This is the first time in the Potash Syndicate's history that such large sales have been made in midsummer. (P. 161)

The Federal Ministry of Food in Germany has agreed to the importation of 200,000 metric tons of Chile **saltpeter** by June 30, 1924, 50 per cent to be used for agriculture and 50 per cent for the fertilizer trade. (P. 161)

The output of **Thomas slag** in Germany during the first three months of 1923, as compared with the same period in 1922, fell off 7 per cent and sales, 30 per cent. (P. 161)

A marked decrease is reported in the sale of German **pharmaceutical** products and the reasons for this decrease are described. (Pp. 161–2)

Germany, in 1922, broke up 10,200,000 tons of raw **limestone.** Of this quantity 2,400,000 tons were sold raw, the remainder being worked up in refining works. (P. 162)

About 1000 tons of **fuel oil** per month are now being used for industrial furnaces in Belgium, and the consumption is increasing at the rate of 100 tons a month. (P. 169)

Great progress has been made in the **tanning** industry in the Union of South Africa in the past ten years, which is described in some detail. (Pp. 171–2)

The production and export of Swedish **paper** and **pulp** during the first six months of 1923 reached quantities exceeding by a considerable margin those for the corresponding period of last year, and comparing even well with so-called normal pre-war years. The cellulose market, while still quiet, is showing signs of improvement under the stimulus of the prospect of an increased demand from Great Britain. (P. 174)

Under the terms of a recent decree of the Royal Hungarian Minister of Finance an **export license** is required for the following articles: alcohol, methylated alcohol; charcoal, peat and peat coal, lignite and coal, coke and all kinds of artificial heating material made thereof; wares of platinum for scientific or industrial use; salt; antimon regulus, sulfur antimon regulus; noxious gases for military purposes; every kind of salts of precious metals; and artificial fertilizers (not made of compound salts) except superphosphates, wood and coal ashes, bone dust, extinct bone charcoal, charcoal fit only for manure, Thomas slag, and other slags. (Pp. 183–4)

The Government of Southern Rhodesia has given notice that until further order a **rebate** of the whole of the **customs duty** shall be granted on the following products: methylated spirits; alcohol of South African manufacture used solely for manufacturing or scientific purposes, or for fuel; South African spirits of a strength of 50 per cent over proof and upward when methylated; South African spirits used for industrial purposes; South African plain spirits used for scientific or teaching institutions for burning, preserving, or experimental purposes; and South African rectified spirit used in the manufacture of ether or ether substances. (P. 186)

The Polish-Silesian **zinc** industry is much concerned with conditions in the Ruhr. The industry mines and smelts local ore but manufactures only semifinished products. (P. 193)

The improvement in the German **paint** and **varnish** industry in the early part of the year proved to be of short duration. Prices advanced beyond the buying power of consumers and a heavy falling off of sales resulted. (P. 214)

A report on the distillation of **alcohol** from "blackstrap" molasses in Cuba has been received in the Chemical Division of the Department of Commerce. Further information may be obtained by addressing that division. (P. 229)

A German company is erecting a factory in Shanghai for the production of **yeast** and chemical products. (P. 229)

A Spanish firm has indicated a desire to import **insulin** from the United States. Further information may be secured by addressing the Chemical Division, Department of Commerce. (P. 229)

The duty on crude **iodine** imported into Tunis has been reduced. (P. 246)

Experiments conducted in Sweden have demonstrated the commercial value of a motor spirit called **"bentyl,"** which is composed of sulfite spirit distilled from the sulfite lye of the wood-pulp mills mixed with 20 to 25 per cent of benzene. As there are now twenty-two sulfite distilleries in Sweden with an annual output of about 20,000,000 liters of 100 per cent alcohol from lye, the new motor fuel may prove to be a serious competitor of imported gasoline. (P. 283)

The situation in the German **chemical industry** is outlined, with particular reference to calcium cyanamide, ammonium sulfate, Chile saltpeter, phosphates and organic nitrogenous fertilizers, soda ash, caustic soda, sulfuric acid, and potash and potash salts. The production of ammonia and chemical fertilizer salts in Germany by the Haber-Bosch process of atmospheric fixation is entirely inadequate for feeding Germany's soil. (P. 287–8)

The **vermilion** industry in Hongkong is reviewed. (P. 288)

During the first six months of 1923 Canada produced $87,152,248 of **minerals,** or an increase of 44 per cent over the output for the corresponding period in 1922. (P. 290)

A new invention for the production of gas from **peat** to be used in the manufacture of glass or in the melting of metal has been reported from Ontario. (P. 294)

A decree of the German Government prohibits the exportation of **minerals** and **mineral oils** except by permits. (Pp. 313–4)

Germany does not require **licenses** for the **exportation** of prepared wax, solid fatty acids, paraffin, and similar candle-making materials; and other manufactures of grease, oil, or wax. (P. 314)

Germany requires **export licenses** for salt, soda, bicarbonates and caustic; aluminium compounds; nitrates of ammonia; lead and soda; acetate of calcium; sulfate of ammonia; metallic acids and salts; chalk; artificial fertilizers. (P. 315)

A German governmental decree **prohibits** the **exportation** of certain essential chemical products of which German production is barely sufficient to cover domestic needs. The chemicals which cannot be exported are listed and include for the most part chemical fertilizer salts, except potash, as well as rock and brine salt, soda ash and caustic soda, artificial alumina, etc. (P. 314)

The prohibition placed upon the exportation of **gum copal** from the Colony of Sierra Leone for a period of three years has expired and the period of prohibition is not to be extended. (Pp. 314–5)

Costa Rica has **reduced** her **import duty** on vegetable waxes, oil of turpentine, paraffin oil, and on nitrobenzene. (P. 315)

A Peruvian decree provides a 10 per cent ad valorem import duty on certain specified chemical **raw materials** required in the Peruvian industry. (P. 315)

STATISTICS OF EXPORTS TO THE UNITED STATES

Brazil—(P 12)
  Manganese ore
Antwerp—(P. 21)
  Gum copal
Straits Settlements—(P. 32)
  Refined tin
Madrid—(P. 32)
  Quicksilver
China—(P. 123)
  Soy-bean oil
  Wood oil
Hungary—(P. 95)
  Oil, fusel
  Stramonium
Malaga—(P. 229)
  Levigated red oxide ore
Belgian Congo—(P. 288)
  Gum copal
Canada—(P. 308)
  Wood pulp
  Pulpwood

SPECIAL SUPPLEMENTS ISSUED

Algeria
Australia
Canada
Danzig
Finland
Hongkong
Indo-China
Portugal
Sweden
Uruguay
Venezuela
Virgin Islands of the United States

Markets for American Pharmaceutical, Medicinal, and Biological Preparations. *Trade Information Bulletin* 149.

Trade-Mark Protection in Europe. *Trade Information Bulletin* 155.

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Foreign and Domestic Commerce

Manzanillo, Mexico, Indigo Dyes. 1 p. *Chemical Trade Bulletin* 1-b. Issued October 25, 1923.

Bureau of Internal Revenue

Denatured Alcohol. Formulas for Completely and Specially Denatured Alcohol. Appendix, *Regulations* 61, Revised. 15 pp. Issued September 21, 1923.

Bureau of Mines

Additions, Removals, and Changes in Permissible List of Explosives from January 1, 1923, to August 31, 1923. J. E. Crawshaw. *Reports of Investigations* 2523. 2 pp. Issued September, 1923.

Air Measurement Methods for Experimental Work on Fan-Pipe Installations. G. E. McElroy and A. S. Richardson. *Reports of Investigations* 2527. 2 pp. Issued September, 1923.

Bibliography of Magnesian Cements. G. H. West, R. L. Sebastian, and W. A. Darrow. *Reports of Investigations* 2534. 17 pp. Issued October, 1923.

Bibliography of Petroleum and Allied Substances, 1921. E. H. Burroughs. *Bulletin* 220. 230 pp. Paper, 20 cents.

Carbon Monoxide Hazards from Tobacco Smoke. G. W. Jones, W. P. Yant, and L. B. Berger. *Reports of Investigations* 2539. 6 pp. Issued October. 1923.

Coal-Mine Fatalities in August, 1923. W. W. Adams. *Reports of Investigations* 2529. 3 pp. Issued September, 1923.

Coal-Mine Fatalities in September, 1923. W. W. Adams. *Reports of Investigations* 2538. 3 pp. Issued October, 1923.

Coke-Oven Accidents in the United States during the Calendar Year 1922. W. W. Adams. *Technical Paper* 349. 37 pp. Paper, 5 cents.

Erection of Barricades during Mine Fires or after Explosions. J. W. Paul, B. O. Pickard, and M W Von Bernewitz. *Miners' Circular* 25. 28 pp. Paper, 5 cents.

Explosives Used in August, 1923. *Reports of Investigations* 2536. 5 pp. Issued October, 1923.

Explosives Used in July, 1923. W. W. Adams. *Reports of Investigations* 2522. 5 pp. Issued September, 1923.

Explosives Used in September, 1923. W. W. Adams. *Reports of Investigations* 2543. 5 pp. Issued November, 1923.

Friction Factors for Fan-Piping Used in Mine Ventilation. G. E. McElroy and A. S. Richardson. *Reports of Investigations* 2540. 3 pp. Issued October, 1923.

Graphites for Brass-Melting Crucibles. R. T. Stull and L. E. Geyer. *Reports of Investigations* 2542. 5 pp. Issued November, 1923.

Manual for Oil and Gas Operations. Including Operating Regulations to Govern the Production of Oil and Gas under the Acts of February 25, 1920, June 4, 1920, and March 4, 1923, and under Special Agreement by the United States. T. E. Swigart and C. E. Beecher. *Bulletin* 232. 145 pp. Paper, 40 cents.

Operating Regulations to Govern Coal-Mining Methods and the Safety and Welfare of Miners on Leased Lands on the Public Domain under the Act of February 25, 1920 (*Public No.* 146), 48 pp. Paper, 5 cents.

Relation of Operating Practice to Composition of Light Oil from Carbureted Water Gas. R. L. Brown, E. F. Pohlman, and H. G. Berger. *Reports of Investigations* 2537. 9 pp. Issued October, 1923.

The Electrothermic Metallurgy of Zinc. B. M. O'Harra. This bulletin represents work done under a coöperative agreement between the Bureau of Mines, Department of the Interior, and the Missouri School of Mines and Metallurgy. *Bulletin* 208. 106 pp. Paper, 15 cents.

The Preparation and Properties of Normal Lead Trinitro Resorcinate. C. A. Taylor and W. H. Rinkenbach. *Reports of Investigations* 2533. 6 pp. Issued October, 1923.

The Transportation of Explosives in and about Mines. (State regulations relating thereto.) L. C. Ilsley. *Reports of Investigations* 2528. 8 pp. Issued September, 1923.

Timbering of Metal Mines. E. A. Holbrook, R. V. Ageton, and H. E. Tufft. *Bulletin* 215. 72 pp. Paper, 25 cents.

Bureau of Standards

Detector for Water Vapor in Closed Pipes. E. R. Weaver and P. G. Ledig. *Technologic Paper* 242. Paper, 5 cents.

Tests of Caustic Magnesia Made from Magnesite from Several Sources. P. H. Bates, R. N. Young, and Paul Rapp. *Technologic Paper* 239. 30 pp. Paper, 10 cents.

United States Government Specification for Gloss Interior Lithopone Paint, White, and Light Tints. *Circular* 147. U. S. Government Standard Specification 67. 8 pp. Paper, 5 cents.

United States Government Specification for Leather Belting. *Circular* 148. U. S. Government Standard Specification 37. 9 pp. Paper, 5 cents.

United States Government Specification for Water-Resisting Red Enamel. *Circular* 146. U. S. Government Standard Specification 66. 6 pp. Paper, 5 cents.

Geological Survey

Coal in 1919, 1920, and 1921. F. G. Tryon and S. A. Hale. Separate from Mineral Resources of the United States, 1921, Part II. 18 pp. Issued October 24, 1923.

Gypsum in 1922. K. W. Cottrell. Separate from Mineral Resources of the United States, 1922, Part II. 7 pp. Published October 18, 1923.

Mineral Resources of the United States, 1920. Part II. Non-Metals. R. W. Stone, geologist in charge. 529 pp. Cloth binding.

Phosphate Rock in 1922. G. R. Mansfield. Separate from Mineral Resources of the United States, 1922, Part II. 24 pp. Published October 16, 1923.

Platinum and Allied Metals in 1922. J. M. Hill. Separate from Mineral Resources of the United States, 1922, Part I. 11 pp. Published October 8, 1923.

Potash in 1922. G. R. Mansfield. Separate from Mineral Resources of the United States, 1922, Part II. 21 pp. Published October 12, 1923.

Silver, Copper, Lead, and Zinc in the Central States in 1922. Mines Report. J. P. Dunlop and F. Begeman. Separate from Mineral Resources of the United States, 1922, Part I. 32 pp. Published October 10, 1923.

Surface Water Supply of the United States, 1921. Part VII. Lower Mississippi River Basin. N. C. Grover, Robert Follansbee, and E. L. Williams. Prepared in coöperation with the States of Colorado, Missouri, and Kansas *Water-Supply Paper* **527.** 39 pp. Paper, 5 cents

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Health Conditions among Chemical Workers, with Respect to Earnings. F. M. Phillips and G. A. Sager. *Public Health Reports* **38** (October 5, 1923), 2320–2.

The Pyrotannic Acid Method for the Quantitative Determination of Carbon Monoxide in Blood and Air. R. R. Sayers, W. P. Yant, and G. W. Jones. *Public Health Reports* **38** (October 5, 1923), 2311–20.

MANUFACTURERS' TECHNICAL PUBLICATIONS

Notice—*Any publications mentioned under this heading will be sent free, unless otherwise noted, to readers of* This Journal, *on request to the firm issuing the publication. When writing for any of these items kindly mention* Industrial and Engineering Chemistry.

Astronomical and Astrophysical Instruments. Descriptive catalog of instruments for this purpose manufactured by the publishers. 48 pp. Wm. Gaertner & Co., Chicago, Ill.

Automatic Temperature Control. *Catalog* **86,** descriptive of indicating, recording, and signaling devices for the automatic control of temperature. 40 pp. Brown Instrument Co., Philadelphia, Pa.

Bailey Boiler Meters. *Bulletin* **42.** Descriptive catalog of these meters and their use. 24 pp. Bailey Meter Co., Cleveland, Ohio.

Biological Laboratory Supplies. *Catalog* **B,** 1923. Catalog of apparatus for bacteriological and biological laboratories. 172 pp. Eimer & Amend, Third Ave., 18th to 19th Sts., New York, N. Y.

Bristol Recording Thermometers and Gages. *Catalog* **1006,** Pressure and Vacuum Gages. 84 pp. *Catalogs* **1102, 1203, 1302,** and **1401,** Recording Thermometer and Pyrometers. 44, 48, and 64 pp. *Bulletin* **289,** Bristol Temperature Controllers. 16 pp. *Preliminary Catalog* **1501** and *Bulletin* **281,** Electrical Recording Voltmeters, Wattmeters, and Ammeters. 32 and 20 pp. *Bulletin* **317,** Tachometers. 34 pp. *Bulletin* **311,** Recording Psychrometers and Humidity Recorders. 12 pp. *Catalog* **717,** Belt Fasteners. 40 pp. The Bristol Co., Waterbury, Conn.

Caldwell Tanks. Descriptive, illustrated catalog and price list of wooden tanks and accessories. 92 pp. W. E. Caldwell & Co., Louisville, Ky.

Castings, Gray, Chemical Iron, and Semisteel. Illustrations of various forms of chemical castings. 48 pp. U. S. Cast Iron Pipe & Foundry Co., Burlington, N. J.

Cenco Hyvac Pump. *Bulletin* **92.** Description of this pump capable of producing vacuum of 0.001 mm. 4 pp. Central Scientific Co., 460 East Ohio St., Chicago, Ill.

Centrifugal Compressors. *Instruction Book* **88,600.** Operating data for multi-stage turbine driven centrifugal compressors for gas exhauster and gas booster service. 62 pp. General Electric Co., Schenectady, N. Y.

Coal, Coke, and By-Products. Standard laboratory tests and apparatus. 36 pp. Scientific Materials Co., Pittsburgh, Pa.

Commercial Minerals. Directory of commercial minerals in Georgia and Alabama along the line of The Central of Georgia Railway. Carefully indexed catalog of the minerals in this particular territory and general map of the territory. 154 pp. Industrial Department, The Central of Georgia Railway Co., Savannah, Ga.

Cross Cracking Process. Technical description of the process and its operation. 16 pp. Gasoline Products Co., 700 Baltimore Ave., Kansas City, Mo.

Crysteel. Descriptive of Crysteel enamels. 32 pp. Crysteel Works, The Benjamin Electric Manufacturing Co., 847 W. Jackson Blvd., Chicago, Ill.

Dunham Vacuum Heating System. *Bulletins* **103** and **110.** Descriptive of the Dunham medium pressure trap and the Dunham heating system. 4 and 12 pp. C. A. Dunham Co., 230 East Ohio St., Chicago, Ill.

Electric Motors. How to Choose Them. 32 pp. Reliance Electric & Engineering Co., Cleveland, Ohio.

Friction Clutches. *Catalog* **1.** Descriptive catalog and price list of friction clutches. 16 pp. W. E. Caldwell Co., Louisville, Ky.

Hardinge Conical Mills. *Catalog* **13,** descriptive of mills and their uses. 32 pp. Hardinge Co., 120 Broadway, New York, N. Y.

Hump Methods for the Heat Treatment of Steel. *Catalog* **90.** Description of methods and instruments used in heat treating. 30 pp. Leeds & Northrup Co., 4901 Stenton Ave., Philadelphia, Pa.

Marcy Ball Mill. *Catalog* **69.** Descriptive catalog of Marcy ball mill with flow sheets. 36 pp. Mine & Smelter Supply Co., Denver, Colo.

Mechanical Fuel Oil Burning Systems. *Bulletin* **16-OA, 16-OG,** and **17-A** Descriptive catalogs of mechanical and low and high-pressure fuel oil burners and a gear pump for viscous liquids. 68 pp. Schutte & Koerting Co., 1239 North 12th St., Philadelphia, Pa.

Microscopes and Bacteriological Materials. Descriptive illustrated catalog. 48 pp. Scientific Materials Co., Pittsburgh, Pa.

Optical Glass. Descriptive manual and catalog with price list of optical glass. 20 pp. Bausch & Lomb Optical Co., Rochester, N. Y.

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Ozone and Electrolytic Water Purifying Apparatus. *Technical Publication* **10.** A concise treatise on the principles, design, and action of U. S. ozonizers and Hartman sterilizers. 35 pp. United States Ozone Co., Scottdale, Pa.

Photomicrography. An introduction to photography with the microscope. 36 pp. Eastman Kodak Co., Rochester, N. Y.

Pneumatic Collecting and Conveying Systems. *Catalog* **291.** Sturtevant fan systems for collecting dust and conveying materials, with tabular data on performance of fans, properties of air, and friction loss in pipes. 72 pp. B. F. Sturtevant Co., Hyde Park, Boston, Mass.

Pyrex Laboratory Glassware. Descriptive catalog and price list. 16 pp. Corning Glass Works, Corning, N. Y.

Reed Air Filters. *Bulletins* **106, 107, 108, 109, 110,** and **111.** Descriptive catalog of Reed filters showing their construction and uses. William Reed Engineering Co., Louisville, Ky.

Rubber. Volume Increase of Compounded Rubber under Strain. Research Bulletin. 12 pp. The New Jersey Zinc Co., 160 Front St., New York, N. Y.

Ruggles-Coles Dryers. *Catalog* **16.** Descriptive catalog of dryers and the particular uses for which they are fitted. 40 pp. Ruggles-Coles Engineering Co., 120 Broadway, New York, N. Y.

Sludge Acid Concentration. *Bulletin* **2.** Description of the Simonson-Mantius vacuum process. 12 pp. Acid Recovery Division, United Lead Co., 111 Broadway, New York, N. Y.

Tag General Catalog. A general catalog of the Tagliabue products consisting of sections dealing with thermometers both indicating and recording, hydrometers, oil-testing instruments, mercurial vacuum gages, pyrometers, Tag-mono flue gas analysis recorders, and automatic controllers of temperature, pressure, humidity, time, liquid level, etc. Also distributed as separate catalogs, dealing with each of these subjects. 216 pp. The C. J. Tagliabue Mfg. Co., 18 Thirty-third St., Brooklyn, N. Y.

Thickening and Clarification. *Bulletin* **12.** Description of the uses of Dorr thickening and clarifying equipment. 24 pp. The Dorr Co., 247 Park Ave., New York, N. Y.

Turboblower. *Catalog* **312.** Itemized data on the Sturtevant turboblower with reference to installation, construction, performance, and operation. 40 pp. B. F. Sturtevant Co., Hyde Park, Boston, Mass.

Water Filters. *Bulletin* **501,** descriptive of Graver horizontal pressure pipe water filters. 12 pp. Graver Corp., East Chicago, Ind.

Wendt's Electro-Titration Apparatus. *Bulletin* **86.** Description of this apparatus and its use with full directions. 12 pp. Central Scientific Co., 460 East Ohio St., Chicago, Ill.

X-Rays. Simple physics of X-ray photography, together with catalog of accessories and operating details. 52 pp. Eastman Kodak Co., Rochester, N. Y.

York Ammonia Fittings and Supplies. 4th edition, 2nd issue. Descriptive illustrated catalog of ammonia-handling equipment, together with tabulated data on the manufacture of ice and artificial refrigeration. 158 pp. York Manufacturing Co., York, Pa.

Zinc as a Paint Pigment. Comparison of various paint pigments. 20 pp. The New Jersey Zinc Co., 160 Front St., New York, N. Y.

MARKET REPORT—NOVEMBER, 1923

[Supplied by Drug & Chemical Markets]

GENERAL conditions in the market for industrial chemicals have shown little change during the month. The total volume of business appears to be increasing gradually, but consumers are still conservative in their purchases and, except for basic materials which will be required during the coming year, are showing no particular desire to enter into contracts. With buying limited to actual requirements, the market remains spotty and prices are unsettled owing to keen competition and excess supplies of stocks on hand. The trend of prices has been slightly downward owing to price revisions in a few basic chemicals.

Perhaps the most interesting event in the market has been the reduction in contract prices of alkalies for the coming year by one of the leading manufacturers of caustic soda and soda ash. While the reduction was not large it was of great interest in the trade, since other manufacturers will no doubt also adjust their prices in line with the new levels. This has been the first change in alkali prices in over two years. The new schedule lists solid caustic, 76 per cent Na_2O, at $3.10 in carlots at works. Soda ash, 58 per cent Na_2O, in bags at $1.38 in carlots. These prices represent a decline of 6$^1/_2$ cents per hundred pounds in caustic and 7 cents in the cases of soda ash. Prices for small quantities in dealers' hands have also been reduced 6 cents in the case of soda ash and 4 cents in caustic soda.

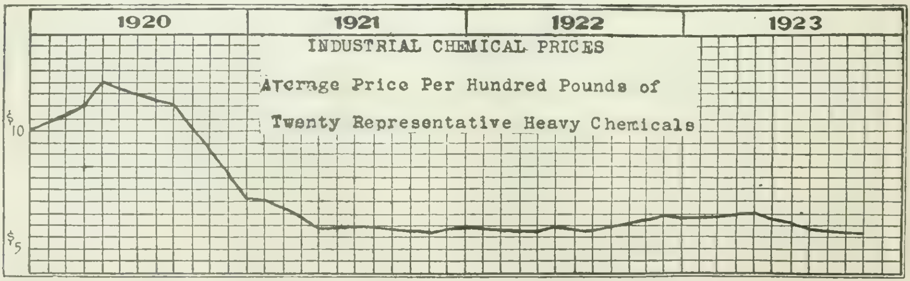
Bleaching powder has been unsettled and prices have been very unstable owing to the keen competition in the market and large production at a time when consumption has been below normal. Announcement was made by one manufacturer of contract prices over 1924 at $1.25 per hundred, f. o. b. works. Prices for the last two months of the year have also been named at $1.25, a reduction of 25c from former quotations. Prices are well below manufacturing costs, but at present the supply appears to be greater than the demand. Advantage is being taken of the low prices for contracts, and business is understood to be improving in this direction. Contract prices for chlorine have also been reduced slightly for large quantities over 1924, a leading maker naming 3$^1/_4$ cents a pound at works.

Arsenic has been very prominent in the market recently. Owing to an apparent world scarcity of arsenic, prices have been advancing steadily from a low of 9 cents per pound during the summer to 14$^1/_2$ cents per pound in November. Domestic producers are reported sold up for the year and are proceeding slowly on deliveries after the first of the year. Japan is offering little this year, while German supplies are limited and are held for high prices, sellers naming 13$^1/_2$ cents per pound for shipment. Consumers were buying freely for a time, but with prices rising rapidly they have withdrawn temporarily.

Sodium prussiate has weakened still further owing to keen competition between imported and domestic producers. Demand has been lacking and prices have been declining steadily. Potassium prussiate is also lower. Copper sulfate has been declining with the fall in copper prices, but is recovering as copper shows signs of recovery. Barium products are stronger, with barium carbonate sold up and chloride quoted at higher prices. Ammonium chloride continues firm. Ammonium sulfate has been weak owing to lack of demand and competition from foreign sources. Acetone is scarce and prices strong. Bichromates have been steady with demand showing some improvement. Sodium sulfide demand has improved, but with supplies abundant prices continue weak. Carbon black has been declining steadily owing to increased supplies and lessened demand. Copper and tin have advanced. Tin crystals are higher. Potassium permanganate is easier. Formaldehyde continues weak. Sulfuric acid is in good demand, but other mineral acids are routine. Oxalic acid is in better demand and higher in price. Formic acid is stronger. Tartaric acid is lower.

Coal-tar crudes have been in good supply and prices have been unsettled. Benzene, especially, has been subject to keen competition among sellers, while the lower prices of gasoline have kept motor benzene prices down. Toluene and solvent naphtha are lower. Phenol has been fairly steady, but with production increasing present prices are showing signs of weakening. Cresylic acid is offered at a range according to grade and quantity. Naphthalene is beginning to move for spring contract deliveries. Prices are about 1 cent per pound lower this year for flake and balls. Pyridine declined sharply following increased supplies from Europe and a lull in demand. Spot prices dropped from $6.00 to $5.00 per gallon. Intermediates have been in routine demand owing to the slow demand for colors. Signs of improvement are in evidence as textile mills begin to resume operations on a broader scale. Makers of β-naphthol have advanced prices following a gradual decline to levels which allowed little or no profit. Aniline oil is steady. Starches and dextrins have receded after two advances due to high cash corn prices.

Changes in vegetable, animal, and fish oil prices have been fewer. Linseed oil has been quiet and prices have been declining. Cottonseed oil has been strong owing to the bullish reports concerning the cotton crop. Corn oil has been strong. Soy bean oil is scarce and higher in price. Animal oils have been fairly steady. Cod and menhaden oils are firm with an upward tendency due to the smaller catches this season. Stearic acid and red oil have been steady. Turpentine is lower. Rosin has been quiet but prices have been fairly steady.



Courtesy of Drug & Chemical Markets

FIRST-HAND PRICES FOR GOODS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET

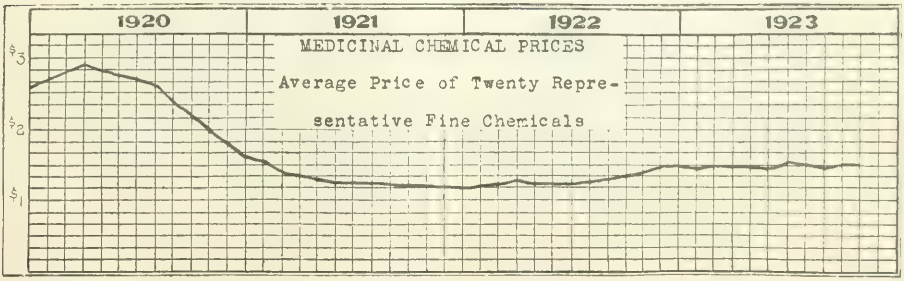
INORGANIC CHEMICALS

	Nov. 1	Nov. 15	Jan. 1923
Acid, Boric, cryst. bbls.......lb.	.11	.11	.11½
Hydrochloric,comm'l. 20° lb.	.01¼	.01¼	.01¼
Hydrofluoric, 30% bbls...lb.	.07	.07	.06
Hydriodic, 10% U. S. P...lb.	.73	.73	.65
Nitric, 42°, cbys. c/1 wks.lb.	.06½	.06½	.06
Phosphoric, 50% tech....lb.	.08	.08	.08
Sulfuric, C. P...........lb.	.09	.09	.07
66° tks. wks.......ton	15.00	15.00	15.00
Oleum, 20%.......ton	19.00	19.00	18.00
Alum, Ammonia, lump.......lb.	.03½	.03½	.03½
Potash, lump...........lb.	*.03¼	*.03¼	*.03½
Chrome............lb.	.05½	.05½	.05½
Soda, ground...........lb.	.04	.04	.04
Aluminum Sulfate (iron-free).lb.	.02½	.02½	.02½
Ammonium Carbonate, pwd..lb.	.09	.09	.09½
Chloride, white gran.....lb.	.07½	.07½	.07½
Ammonia, anhydrous........lb.	.30	.30	.30
Ammonia Water, drums, 26°.lb.	.07½	.07½	.07½
Arsenic, white..............lb.	.14	.14¼	.15½
Barium Choride............ton	*82.50	*82.50	*92.50
Nitrate................lb.	*.07½	*.07½	*.07½
Barytes, white.............ton	33.50	33.50	33.50
Bleaching Powd., 35%, works .... 100 lbs.	1.50	1.35	2.15
Borax, cryst., bbls...........lb.	.05¾	.05¾	.05½
Bromine, pure, wks...........lb.	.29	.29	.29
Calcium Chloride, fused, f.o.b. N. Y.................ton	24.50	24.50	24.50
Chlorine, liquid.............lb.	.05½	.05½	.05¼
Copper Sulfate......... 100 lbs.	4.90	4.80	6.25
Iodine, resublimed...........lb.	4.55	4.55	4.50
Lead Acetate, white crystals..lb.	.14	.14	.13
Nitrate................lb.	.22	.22	.22
Red.............. 100 lbs.	11.40	11.40	10.60
White (Carb.)..........lb.	.09¾	.09¾	.08½
Lime, live and hydrated, bbl..lb.	.01½	.01½	.01½
Oyster shell.............lb.	.03½	.03½	.03
Lime Acetate.......... 100 lbs.	4.00	4.00	3.50
Magnesium Carbonate, tech..lb.	.08	.08	.08
Magnesite, calcined.........ton	55.00	55.00	55.00
Phosphorus, yellow..........lb.	.35	.35	.32
Red...................lb.	.75	.75	*.30
Plaster of Paris, tech ....bbl.	3.30	3.30	3.30
Potassium Bichromate.......lb.	.09½	.09½	.10
Bromide, imported......lb.	.17	*.17	.14½
Carbonate, calc.,80–85%.lb.	*.06½	*.06½	*.05½
Chlorate, cryst..........lb.	*.07½	*.07½	*.05½
Hydroxide, 88–92%.....lb.	*.07	*.07	*.08
Iodide, bulk, U. S. P.....lb.	3.75	3.75	3.60
Nitrate................lb.	.06½	.06½	.06½
Permanganate, U. S. P...lb.	*.17½	*.17¾	*.16
Prussiate, red..........lb.	*.60	*.60	*.90
Yellow............lb.	*.30	*.29	*.38
Salt Cake, bulk............ton	24.00	24.00	28.00
Silver Nitrate...............oz.	.44	.44	.44
Soda Ash, 58%, bags....100 lbs.	*2.00	*1.94	*2.00
Caustic, 76%, N. Y. 100 lbs.	3.70	3.66	3.50
Sodium Acetate.............lb.	.05	.05	.07¼
Bicarbonate....... 100 lbs.	2.25	2.25	2.00
Bichromate.............lb.	.07⅛	.07⅛	.07¾
Bisulfite, powd..........lb.	.04½	.04½	.04
Chlorate...............lb.	.06½	.06½	.06½
Cyanide, 96–98%.......lb.	.23	.23	.23
Fluoride, tech..........lb.	.09	.09	.09½
Hyposulfite, bbls... 100 lbs.	2.75	2.75	3.60
Nitrate, 95%...... 100 lbs.	2.45	2.45	2.57½
Nitrite.................lb.	.07¼	.07¼	.08½
Prussiate, yellow........lb.	.13	.13	.18½
Phosphate (di-sod.), tech.lb.	.03½	.03½	.03½
Silicate, 40° ....100 lbs.	.80	.80	.80
Sulfide, 60%, fused......lb.	.04½	.04½	.05
Strontium Nitrate...........lb.	*.10	*.10	*.08¾
Sulfur, flowers.........100 lbs.	3.00	3.00	3.00
Crude, mines......long ton	14.00	14.00	14.00
Tin Bichloride, 50% sol'n....lb.	.13	.13	.10¼
Oxide..................lb.	.47	.47	.43
Zinc Chloride, U. S. P........lb.	.25	.25	.20
Oxide, bbls.............lb.	.08½	.08½	.07½

* Resale or Imported (not an American maker's price).

ORGANIC CHEMICALS

	Nov. 1	Nov. 15	Jan. 1923
Acetanilide, U. S. P., bbls....lb.	.32	.32	.35
Acid, Acetic, 28 p. c.... 100 lbs.	3.38	3.38	3.17½
Glacial ....100 lbs.	12.78	12.78	12.05
Benzoic, U. S. P.........lb.	.72	.72	.72
Carbolic, cryst., U. S. P., drums.............lb.	.26	.26	.32
50- to 110-lb. tins...lb.	.30	.28	.34
Citric, crystals, kegs.....lb.	*.50	*.50	*.48½
Oxalic, cryst., bbls., wks.lb.	.11¾	.12	.13½
Pyrogallic, resublimed...lb.	1.55	1.55	1.55
Salicylic, U. S. P.........lb.	.35	.35	.45
Tannic, U. S. P., bbls....lb.	.83	.83	.70
Tartaric, cryst., U. S. P...lb.	*.29	*.29	*.32
Acetone, drums.............lb.	.25	.25	.21
Alcohol,denatured, complete. gal.	.46	.46	.45
Ethyl, 190 proof, bbls...gal.	4.75	4.75	4.70
Amyl Acetate............. gal.	4.50	4.50	2.50
Camphor, Jap, refined, cases .lb.	.86	.86	.86
Carbon Bisulfide, c/1........lb.	.06	.06	.06
Tetrachloride...........lb.	.10½	.10½	.10½
Chloroform, U. S. P., drums..lb.	.35	.35	.35
Creosote, U. S. P...........lb.	.40	.40	.40
Cresol, U. S. P..............lb.	.25	.25	.25
Dextrin, corn ....100 lbs.	4.09	3.84	3.09
Imported Potato........lb.	.07½	.07½	.09
Ether, U. S. P., 100 lbs.......lb.	.13	.13	.13
Formaldehyde, bbls..........lb.	.11	.11	.16
Glycerol, dynamite, drums...lb.	.16½	.16½	.16½
Methanol, pure, drums......gal.	1.00	1.00	1.35
Methylene Blue, med........lb.	2.25	2.25	2.25
Petrolatum, light amber......lb.	.04½	.04½	.03¾
Pyridine ....gal.	6.00	4.50	2.75
Starch, corn, pow'd.....100 lbs.	3.69	3.44	2.47
Potato, Jap.............lb.	.06	.06	.06¾
Sago....................lb.	.05	.05	.03½



Courtesy of Drug & Chemical Markets

OILS, WAXES, ETC.

	Nov. 1	Nov. 15	Jan. 1923
Beeswax, pure, white.........lb.	.36	.36	.36
Castor Oil, No. 3............lb.	.13	.13½	.13
Ceresin, yellow..............lb.	.08	.08	.08½
Corn Oil, crude, tanks, mills...lb.	.09¾	.10¼	.09¾
Cottonseed Oil, crude, f. o. b. mill ....lb.	.10	.10	.09⅝
Linseed Oil, raw, lc/l........gal.	.92	.90	.87
Menhaden Oil, crude, mills...gal.	.47½	.50	.53
Neat's-foot Oil, 20°..........lb.	.16½	.16½	.18½
Paraffin, 128–130 m. p., ref....lb.	.04	.04	.04
Rosin, "F" grade, 280 lbs....bbl.	5.80	5.80	6.25
Rosin Oil, first run..........gal.	.43	.43	.45
Shellac, T. N................lb.	.62	.62	.80
Sperm Oil, bleached winter, 38°....................gal.	.99	.99	1.03
Stearic Acid, double pressed...lb.	.13	.13	.12½
Tallow Oil, acidless..........lb.	.09½	.10⅛	.11½
Turpentine, spirits of........gal.	.99	.95	1.56

METALS

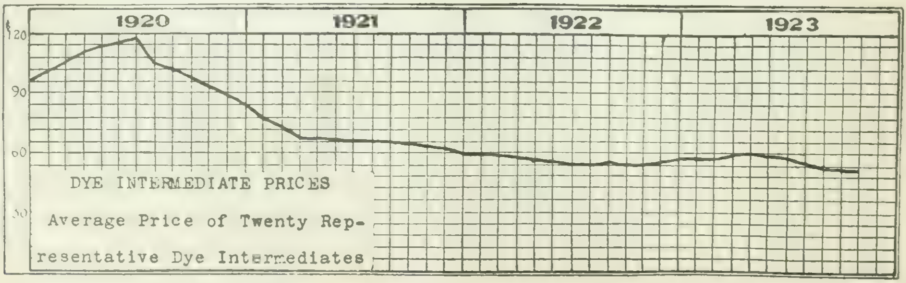
	Nov. 1	Nov. 15	Jan. 1923
Aluminium, No. 1, ingots.....lb.	.25	.25	.23
Antimony, ordinary......100 lbs.	8.50	9.25	6.75
Bismuth....................lb.	2.75	2.75	2.75
Copper, electrolytic..........lb.	.12½	.13¼	.14¾
Lake....................lb.	.12¾	.13½	.14¾
Lead, N. Y.............100 lbs.	6.75	6.75	7.80
Nickel, electrolytic..........lb.	.29	.29	.36
Platinum, refined, soft........oz.	116.00	116.00	118.00
Quicksilver, flask......75 lbs. ea.	61.00	61.00	73.00
Silver, foreign...............oz.	.63½	.63¼	.63
Tin........................lb.	.41½	.43⅜	.39
Tungsten Wolframite....per unit	8.50	8.50	7.50
Zinc, N. Y.............100 lbs.	6.65	6.80	8.25

FERTILIZER MATERIALS

	Nov. 1	Nov. 15	Jan. 1923
Ammonium Sulfate, expt.100 lbs.	3.40	3.40	3.90
Blood, dried, f. o. b. N. Y...unit	4.00	4.00	4.70
Bone, 3 and 50, ground, raw..ton	25.00	25.00	28.00
Calcium Cyanamide, unit of ammonia..................	2.25	2.25	2.25
Fish Scrap, dried, wks.......unit	4.10	4.10	5.35 & .10
Phosphate Rock, f. o. b. mine:			
Florida Pebble, 68%.....ton	3.25	3.25	3.00
Florida, 70%...........ton	3.55	3.55	3.55
Florida, 74–75%........ton	4.50	4.50	4.50
Tennessee, 72%.........ton	5.50	5.50	5.25
Potassium Muriate, 80%....unit	.68	.68	.68
Tankage, high-grade, f. o. b. Chicago...............unit	3.75 & .10	3.75 & .10	4.75 & .10

COAL-TAR CHEMICALS

	Nov. 1	Nov. 15	Jan. 1923
Crudes			
Anthracene, 80–85%.........lb.	.75	.75	.75
Benzene, pure, tanks........gal.	.23	.23	.30
Naphthalene, flake...........lb.	.06½	.06½	.06½
Phenol, drums...............lb.	.26	.26	.32
Crudes *(concluded)*			
Toluene, pure, tanks.........gal.	.26	.26	.30
Xylene, 2 deg. dist. range, drums.................gal.	.50	.50	—
Intermediates			
Acids:			
Anthranilic..............lb.	.96	.96	1.10
Benzoic, tech............lb.	.70	.70	.65
Cleve's.................lb.	1.00	1.00	1.25
Gamma..................lb.	1.70	1.70	1.85
H......................lb.	.75	.75	.80
Metanilic...............lb.	.60	.60	.60
Monosulfonic F..........lb.	2.30	2.30	2.30
Naphthionic, crude.......lb.	.62	.62	.60
Nevile & Winther's.......lb.	1.15	1.15	1.15
Picric..................lb.	.25	.25	.20
Sulfanilic...............lb.	.20	.20	.19
Tobias'.................lb.	1.10	1.10	1.30
Aminoazobenzene............lb.	1.15	1.15	1.15
Aniline Oil..................lb.	.16½	.16½	.17
Aniline Salt.................lb.	.24	.24	.25
Anthraquinone (sublimed).....lb.	1.30	1.30	1.30
Benzaldehyde, tech...........lb.	.75	.75	.65
U. S. P..................lb.	1.50	1.50	1.40
Benzidine Base...............lb.	.82	.82	.84
Benzidine Sulfate............lb.	.70	.70	.70
Diaminophenol...............lb.	3.80	3.80	3.75
Dianisidine..................lb.	4.60	4.60	4.50
p-Dichlorobenzene...........lb.	.17	.17	.17
Diethylaniline...............lb.	.60	.60	.60
Dimethylaniline..............lb.	.41	.41	.41
Dinitrobenzene...............lb.	.19	.19	.19
Dinitrotoluene...............lb.	.19	.19	.20
Diphenylamine...............lb.	.48	.48	.50
G Salt......................lb.	.55	.55	.60
Hydroquinol.................lb.	1.25	1.25	1.05
Monochlorobenzene..........lb.	.10	.10	.10
Monoethylaniline............lb.	1.00	1.00	1.00
b-Naphthol, dist.............lb.	.26	.26	.26
a-Naphthylamine............lb.	.35	.35	.29
b-Naphthylamine............lb.	.75	.75	.95
m-Nitroaniline...............lb.	.78	.78	.80
p-Nitroaniline...............lb.	.74	.74	.74
Nitrobenzene (Oil Mirbane)...lb.	.10	.10	.10
p-Nitrophenol...............lb.	.75	.75	.72
o-Nitrotoluene...............lb.	.09	.09	.10
p-Nitrotoluene...............lb.	.50	.50	.65
m-Phenylenediamine..........lb.	.96	.96	1.00
p-Phenylenediamine..........lb.	1.45	1.45	1.50
Phthalic Anhydride..........lb.	.25	.25	.35
R Salt......................lb.	.55	.55	.55
Resorcinol, tech.............lb.	1.40	1.40	1.50
U. S. P.................lb.	2.25	2.25	2.00
Schaeffer's Salt.............lb.	.60	.60	.60
Sodium Naphthionate........lb.	.62	.62	.62
Thiocarbanilide.............lb.	.35	.28	.35
Tolidine (base)..............lb.	.95	.95	.95
Toluidine, mixed............lb.	.31	.31	.30
o-Toluidine..................lb.	.16	.16	.15
p-Toluidine..................lb.	.90	.90	1.00
m-Toluylenediamine..........lb.	.90	.90	.95
Xylidine.....................lb.	.50	.50	.42



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